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X-RAY OPTICS

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*The Diffraction of X-rays by
Finite and Imperfect Crystals*

by

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PREFACE

THE simpler observations in X-ray crystallography can be treated on the idea that X-rays are reflected from layers of atoms in the crystal, and that the beams reflected by successive parallel layers interfere with one another. This was sufficient, for example, for the interpretation of the early ionization-spectrometer measurements, and of the Laue photographs of simple substances. When more complex crystals were studied some means of exhibiting neatly the information given by the large numbers of spots on moving-crystal and moving-crystal moving-film photographs were necessary, and the device known as the reciprocal lattice was found convenient for this purpose. This device is indeed almost a necessity for the interpretation of such photographs. The reciprocal lattice is not generally familiar, and many books on crystallography stop short at the point where its use becomes desirable. This point is roughly the division between one-dimensional and three-dimensional problems in X-ray optics. Some of the latter problems are treated here: the construction and properties of the reciprocal lattice, its relation to the commoner types of X-ray diffraction photograph, the representation in reciprocal space of crystals that are small, distorted or otherwise imperfect, and the effects of the imperfections on X-ray photographs. The chapter on the effects of thermal agitation on X-ray diffraction is included with some misgivings, since the writer has no first-hand acquaintance with it. One subject that would naturally form part of X-ray Optics is omitted: the use of

Fourier series in the investigation of crystal structures. The omission is partly because of the considerable space that would be required to deal with it usefully, and partly because, in the no-man's-land of Crystallography, structure determination is definitely closer to Chemistry than to Physics.

It is hoped that a satisfactory compromise has been struck between the diffuseness of a non-mathematical treatment and the uninviting symbolism of some of the original papers. The necessary mathematics is introduced gradually, the earlier chapters requiring little more than elementary trigonometry. The monographs *X-rays* and *X-ray Crystallography* in this series have been kept in mind, and it will be found that there is practically no overlapping in treatment and very little of topic.

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CHAPTER I

INTRODUCTION

1. IDEALLY, a crystal* is an arrangement of atoms that repeats itself indefinitely in three dimensions. The repeating group of atoms occupies a small parallelepiped, called the unit cell. The edges of the unit cell are the crystal axes, and are generally represented by the letters a , b , c . The parallelepiped is not necessarily rectangular, and the angles between the pairs of axes are denoted α , β , γ (figure 1).

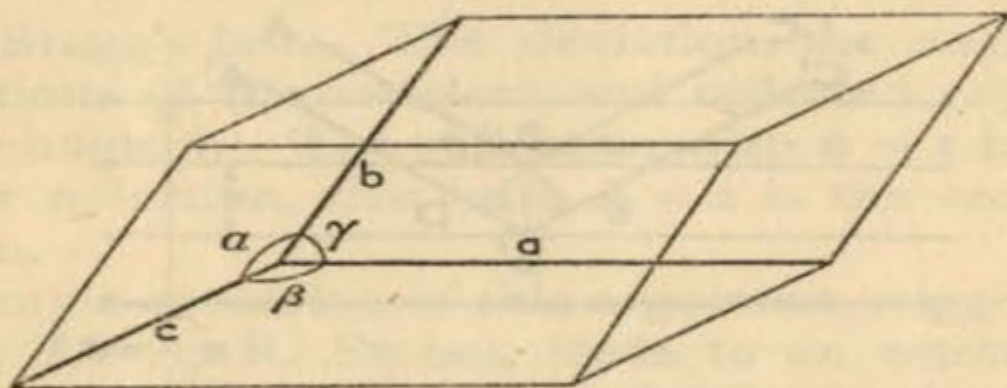


FIG. 1.—Axes and angles of a unit cell.

The complete crystal is made by the regular packing together of these units, and the network formed by the edges of the unit cells is called the crystal lattice. In most crystals the atoms within the unit cell are arranged according to certain geometrical rules of symmetry that govern the positions of equivalent atoms. It can be shown that there are exactly two hundred and thirty sets of rules possible. They are known as space groups, and are of fundamental importance in crystal structure analysis. A really perfect crystal would be of infinite size, as the periodicity necessarily stops at the crystal boundaries, but

* Fuller descriptions and more precise definitions of the technical terms introduced in this paragraph will be found, for example, in *The Crystalline State*, by W. L. Bragg (Bell, London, 1933), or in *X-Ray Crystallography*, by R. W. James.

for most purposes a crystal of more than a thousandth of a centimetre in linear dimensions can be considered perfect. The main interest of this book is in the diffraction effects produced in X-ray photographs of a crystal in which something has gone wrong—its size too small, or the lattice-network curved, or the space-group rules only approximately obeyed.

2. It is convenient to begin by recalling some results that can be obtained without the use of the reciprocal lattice. The first of these is Bragg's law. In deriving this law it is postulated that a crystal consists of parallel planes of atoms whose arrangement repeats at regular

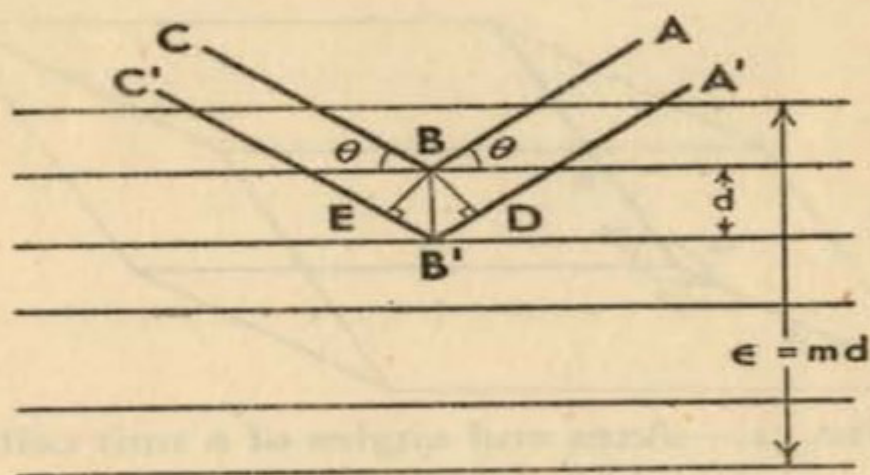


FIG. 2.—Derivation of Bragg's law and estimation of the angular range of reflection.

intervals d (figure 2). Such atomic planes are very evident when a model of some simple crystal is examined, and may be picked out in many different ways. These planes are each supposed to reflect a certain small fraction of the incident beam of X-rays, so that the angle θ between the incident rays and the planes is equal to the angle between the reflected rays and the planes, and so that the incident and reflected rays lie in the same plane. For an arbitrary angle θ the reflected intensity is small, as there is then no special phase relation between the reflections from successive planes, and the reflected rays largely cancel one another. For certain angles, however, the extra distance

travelled by the ray $A'B'C'$ will be an integral number of wave-lengths greater than that travelled by the ray ABC , and the reflected rays reinforce one another. It is easy to see that, if this condition is fulfilled for the pair of rays ABC and $A'B'C'$, it is fulfilled for all other rays, and a strong reflected beam is produced. If BD and BE are the perpendiculars from B on $A'B'$ and $C'B'$, the extra distance travelled is $DB' + B'E$, and reinforcement occurs if this distance is $n\lambda$, where n is any integer and λ is the wave-length of the monochromatic incident X-rays. The lengths of DB' and $B'E$ are each $d \sin \theta$, so the beam is strongly reflected when

$$2d \sin \theta = n\lambda, \quad . \quad . \quad . \quad (1)$$

which is Bragg's law. The deviation, the angle between the directions of the incident and reflected rays, is twice the Bragg angle θ . The reflection with $n = 1$ is called the first-order reflection, that with $n = 2$ is the second order, and so on.

3. A simple extension of this argument, suggested to the writer by Dr A. R. Stokes, leads to an estimate of the angle β over which the intensity of reflection is appreciable. At the angle given by equation (1) all the planes are reflecting so that their contributions add, but the contribution of the last plane is actually mn wave-lengths out of phase with that of the first. If it were $mn + 1$ or $mn - 1$ wave-lengths out of phase the intensity of reflection would be zero, since the contribution of the top half of the crystal would be cancelled by the contribution of the bottom half. As a rough estimate the range of θ over which the intensity of reflection is appreciable may be taken as half the difference between the angles giving these phase relationships. If

$$2\varepsilon \sin \theta' = (mn + 1)\lambda,$$

$$2\varepsilon \sin \theta'' = (mn - 1)\lambda,$$

$$\varepsilon(\sin \theta' - \sin \theta'') = \lambda,$$

$$2\varepsilon \cos \frac{\theta' + \theta''}{2} \sin \frac{\theta' - \theta''}{2} = \lambda,$$

or, since θ' and θ'' differ very little from θ ,

$$\theta' - \theta'' = \lambda/\varepsilon \cos \theta,$$

where $\varepsilon = md$ is the thickness of the crystal. If ε is small (less than about 10^{-4} cm.), $(\theta' - \theta'')$ is quite appreciable, and the crystal reflects over a small range on either side of the angle given by equation (1). The effect is analogous to the imperfect resolution given by diffraction gratings of few lines. Since the actual deviation of the rays is 2θ , the range of deviation over which the intensity is appreciable is $(\theta' - \theta'')$, or

$$\beta \sim \lambda/\varepsilon \cos \theta. \quad . \quad . \quad . \quad (2)$$

This argument gives only the order of magnitude of β , but the proportionality factor is not far from unity, and it is convenient to define the 'apparent particle size' of a crystal by

$$\varepsilon \equiv \lambda/\beta \cos \theta. \quad . \quad . \quad . \quad (3)$$

The intensity of reflection does not, of course, remain constant over an angular range β and then drop suddenly to zero. A more precise definition of β in terms of the measured variation of intensity of reflection with angle is given in chapter II, and its variation with the shape and orientation of the crystal particle is discussed in chapter IV.

4. If the crystal is larger than 10^{-4} cm., reflection may still take place over a considerable range if the crystal is otherwise imperfect. For example, in a distorted crystal the interplanar spacing d will not be constant throughout, and different parts of the crystal will reflect at different angles. The broadening of the lines on powder photographs of an aggregate of such distorted crystals may be estimated from equation (1). If the maximum strain in the crystal is e , the spacing will vary from $d(1 + e)$ to $d(1 - e)$, and θ will vary over a range numerically equal to $2ed(\partial\theta/\partial d)$, or $2e \tan \theta$. Since the deviation of the rays

is 2θ , the range of angle over which the reflection is appreciable will be twice this, or

$$\beta \sim 4e \tan \theta. \quad (4)$$

In cases of broadening from this cause it is convenient to define the 'apparent strain' by

$$\eta \equiv \beta \cot \theta. \quad (5)$$

Equation 4 suggests that the apparent strain is about four times the maximum strain. The relation between actual and apparent strain is treated in chapter VIII, but the problem is not in as satisfactory a state as that of the broadening due to small crystal size.

5. The other forms of crystal imperfection do not lend themselves to elementary treatment, and it seems best to postpone discussion of them to later chapters.

CHAPTER II

X-RAY DIFFRACTION AND THE RECIPROCAL LATTICE

1. THE derivation of the Bragg law given above is simple, but it has certain weaknesses. Aesthetically it is displeasing, because it is a mixture of geometrical and physical optics. The interaction of the X-rays with a single plane of atoms is treated by geometrical optics, as simple reflection, while the interaction with successive planes is treated by physical optics, as interference. It is by no means obvious why a single plane of atoms ought to reflect X-rays as a mirror reflects light; we shall see shortly that in fact it would not. Also, in complex structures, where there are atoms in 'general' positions in the unit cell (that is, atoms whose positions are not determined completely by symmetry) the successive planes of atoms postulated are no longer evident, and the treatment loses its plausibility. We must therefore make a new start on the problem of the interaction of X-rays and crystals, using physical optics throughout, and treating the whole crystal impartially, with no bias toward planes and interplanar spaces. This will lead naturally to the important concepts of reciprocal space and the reciprocal lattice, which form the basis of modern X-ray crystallography.

2. Suppose first that each unit cell contains a single scattering centre. This may be imagined as a single atom, or as the centre of gravity of the actual distribution of electrons in the unit cell. The fact that all the electrons are not at the centre of gravity is an additional complication, which fortunately can be treated separately as the 'structure amplitude' (James, pp. 49-53, and below, p. 45), and for the present it is better to ignore it. In figure 1 the dots represent the scattering centres in the plane containing the a and b axes of the crystal, and AB represents the direction

of a parallel beam of monochromatic X-rays falling on it. In general, each scattering centre will diffract rays in all directions, the amplitude depending on the relation between the direction of the incident ray AB and the direction of the diffracted ray BC , but there will be some radiation diffracted in every direction. Most of the diffracted radiation is 'coherent' with the incident beam, that is the phase of the vibration of the diffracted ray BC is fixed by the phase of the vibration of the incident ray AB . The total amplitude of the radiation diffracted in the direction BC will therefore be the sum of the contributions of the individual scattering centres, proper attention being paid to

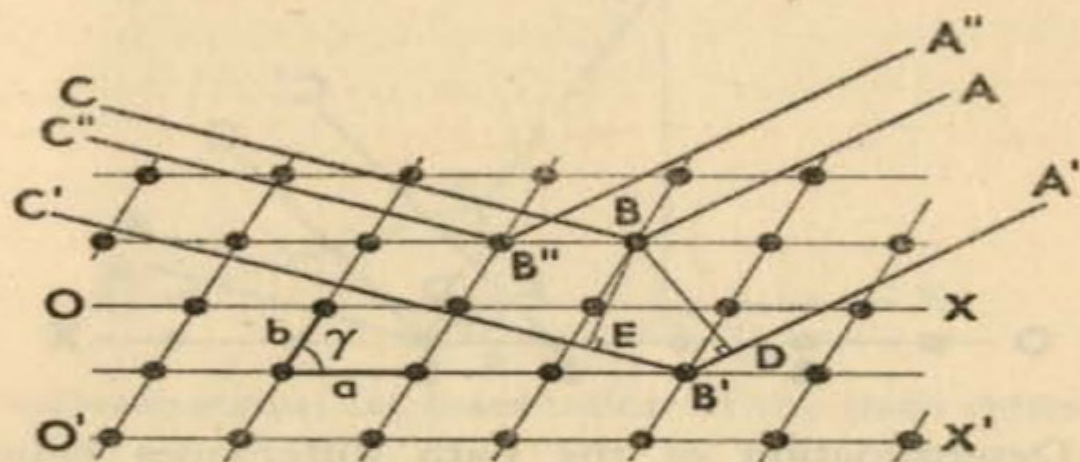


FIG. 1.—X-rays diffracted by a plane of scattering centres.

the phase relations. If it happens that for every scattering centre B, B', B'', \dots the scattered rays $BC, B'C', B''C'', \dots$ are in phase the radiation diffracted in the direction BC will be of great intensity, since all the contributions add. On the other hand, if there is no particular relation between the phases of the rays $BC, B'C', B''C'', \dots$ the radiation will be weak, as the contributions of the various scattering centres will mostly cancel each other out. The condition that the ray BC and the ray $B'C'$ should add is clearly that $B'D + B'E$ should be an integral multiple of λ , where BD and BE are perpendicular to $A'B'$ and $B'C'$ respectively, and λ is the wave-length of the incident X-rays.

Our object is to find a simple geometrical way of representing the fulfilment of this condition for every scattering centre of the crystal. This is best done in stages, a line of scattering centres being considered first, then a plane, and finally the whole crystal. It is convenient, though not necessary, to take the line parallel to one of the crystal axes, say a , and the plane including two of the crystal axes, say a and b .

In figure 2, then, OX represents a line of scattering centres, at a constant distance a apart. The contributions of the scattering centres B and B' will add if the path difference $B'D + B'E = h\lambda$, where h is any integer, positive, negative, or zero. (The figure is drawn for h positive; the

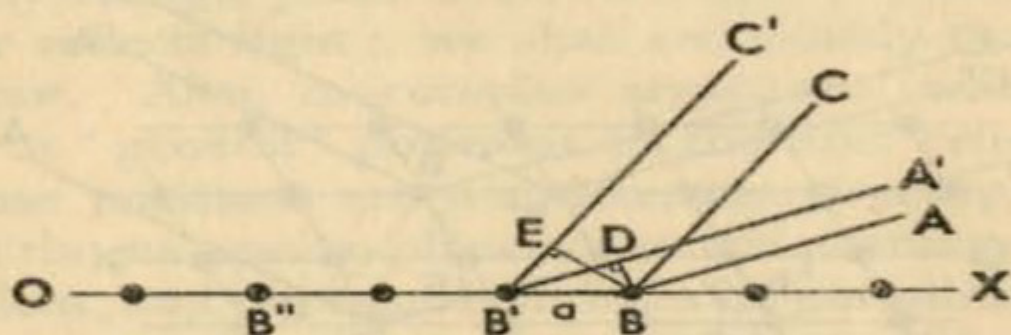


FIG. 2.—Determination of the path differences between rays diffracted by successive scattering centres in a line.

reader should convince himself that the condition holds for other directions of AB and BC . The lines AB , BC and OX are not necessarily coplanar.) A little consideration shows that if the contributions of the adjacent scattering centres B and B' add, the contribution for any other scattering centre B'' in the row will add also, the path difference for B and B'' being an integral multiple of that for B and B' . The condition that $B'D + B'E = h\lambda$ can be represented as follows. From a fixed origin O (figure 3) draw a straight line of unit length OP parallel to BA , and from P draw a straight line of unit length PQ parallel to BC . Let PP' and QQ' be perpendiculars from P and Q on OX , where OX is parallel to the line of scattering centres. Then the

triangle $OP'P$ (figure 3) is similar to the triangle $B'DD$ (figure 2), since their angles are equal, and so

$$\frac{OP'}{B'D} = \frac{OP}{B'B} = \frac{1}{a},$$

$$OP' = B'D/a.$$

Similarly
so that

$$P'Q' = B'E/a,$$

$$OP' + P'Q' = OQ' = (B'D + B'E)/a = h\lambda/a$$

is the condition that the rays diffracted by all the scattering centres B, B', B'', \dots add. Interpreted geometrically,

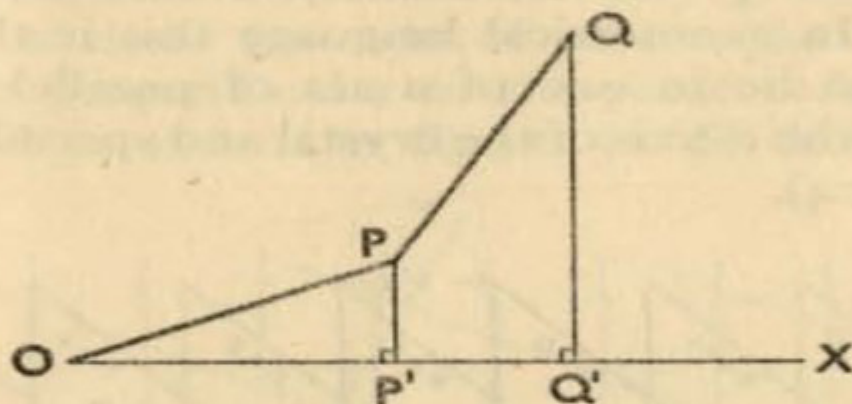


FIG. 3.—Geometrical representation of the path differences.

$OQ' = h\lambda/a$ is the condition that Q should lie in a plane perpendicular to OX and distant $h\lambda/a$ from O . The radiation diffracted by the line of scattering centres has therefore its greatest possible intensity if Q lies in one of a set of parallel planes perpendicular to the line of scattering centres and separated λ/a from one another. As Q moves away from one of these planes the intensity of the diffracted radiation will fall off, and will become inappreciable at a distance of the order of λ/t from the plane, where t is the length of the line of scattering centres. This is of course small compared with λ/a , and for many purposes can be neglected. The falling off in intensity is caused by the rays diffracted by the various scattering centres becoming out of phase with one another, and will be considered in detail in the next chapter.

3. The representation of the condition for reinforcement that has just been derived is satisfactory for diffraction of X-rays of a single wave-length λ , but for some uses the dependence of the spacing of the planes on λ is inconvenient. This may, however, be avoided by a simple device. The lengths of OP and PQ were taken as unity, as any other choice would have seemed artificial as a starting-point, but any convenient length may be substituted. If the length $1/\lambda$ is chosen for OP and PQ , OP' becomes $B'D/\lambda a$, $P'Q'$ becomes $B'E/\lambda a$ and $OQ' = OP' + P'Q'$ becomes $(B'D + B'E)/\lambda a$. The condition for reinforcement is therefore that OQ' should be equal to h/a , where h is an integer. In geometrical language this is the condition that Q should lie in one of a set of parallel planes perpendicular to the a -axis of the crystal and spaced at distances of $1/a$ (figure 4).

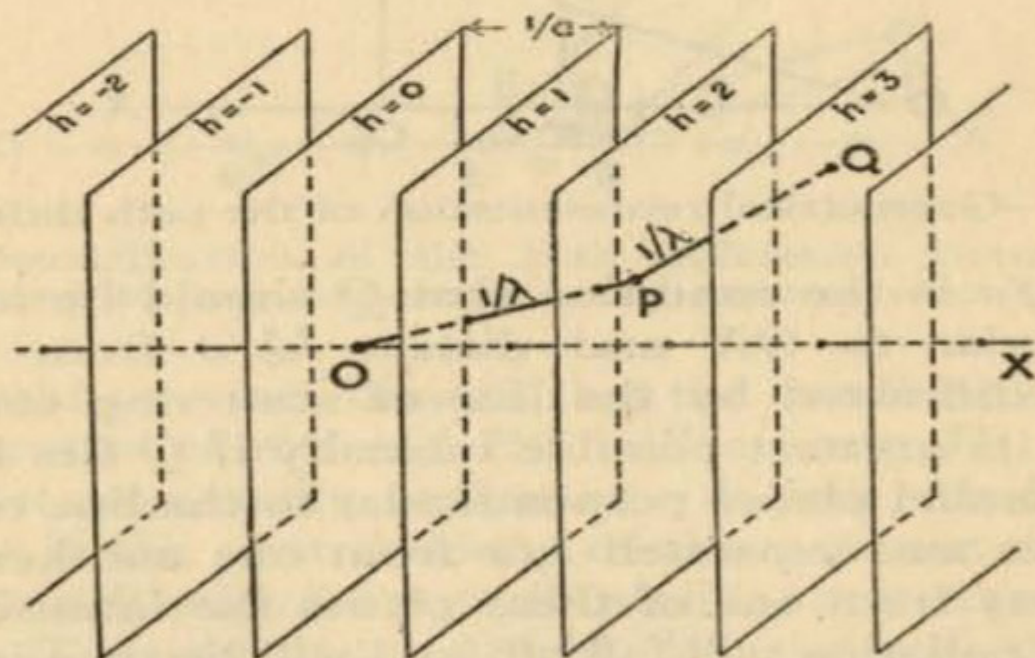


FIG. 4.—Condition that the path differences should be integral multiples of the wave-length.

4. The condition so far derived relates only to a single line of scattering centres OX . However, if it is satisfied for one line OX , it is satisfied for any parallel line $O'X'$ (figure 1), since all arguments have involved only the

directions of rays, and not the absolute positions of the scattering centres. The line OX of figure 1 could be translated bodily to the position $O'X'$ without affecting the directions of any of the rays in succeeding figures. The case is different with regard to lines of scattering centres not parallel to OX . Application of the same argument to a line of scattering centres parallel to the b -axis of the crystal gives as the condition for the reinforcement of the scattered rays that Q should lie on one, say the k^{th} , of a set of parallel planes perpendicular to the b -axis and spaced a distance $1/b$ apart. If the two conditions for reinforcement are to be satisfied simultaneously Q must lie on the intersection of these two sets of planes, that is on one of a set of lines perpendicular to the plane containing a and b and spaced as shown in figure 5. If this condition is

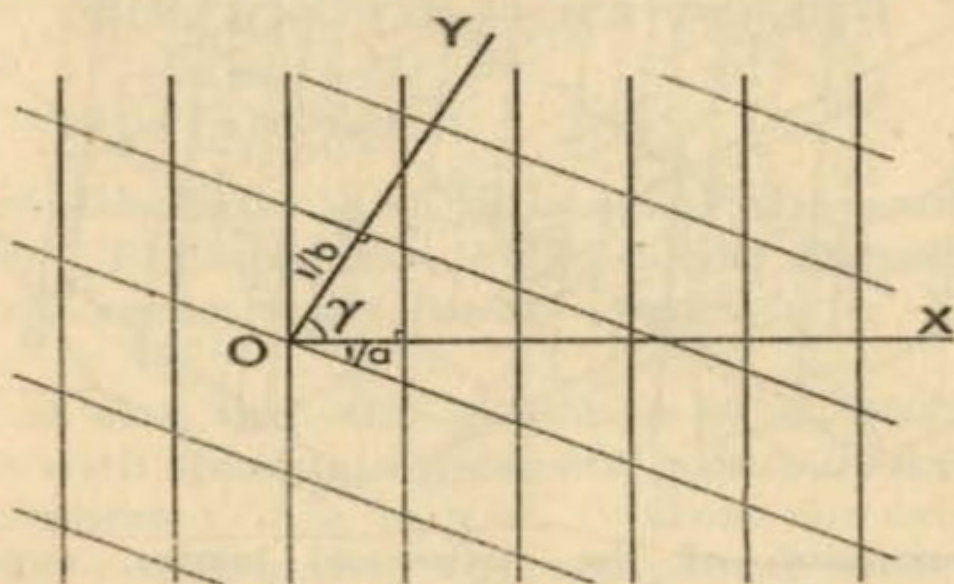


FIG. 5.—Condition that the path differences between rays diffracted by all scattering centres in a plane should be integral multiples of the wave-length.

satisfied all centres in the plane shown in figure 1 scatter in phase, and the diffracted radiation is of maximum intensity. This behaviour is different from that assumed in the derivation of Bragg's law given in chapter I. A little consideration makes it clear that reflection as if by a mirror corresponds only to the vertical line through the origin in figure 5.

If all the scattering centres of the crystal are to diffract in phase, a similar condition for the reinforcement of the rays scattered by a line of centres in the direction of the c -axis must also be fulfilled. As now seems natural, the condition is that Q should lie on one, say the l^{th} , of a set of parallel planes perpendicular to the c -axis and spaced a distance $1/c$ apart. These will intersect the vertical lines of figure 5 in a series of points, forming a new lattice (figure 6), and all the unit cells of the crystal will scatter

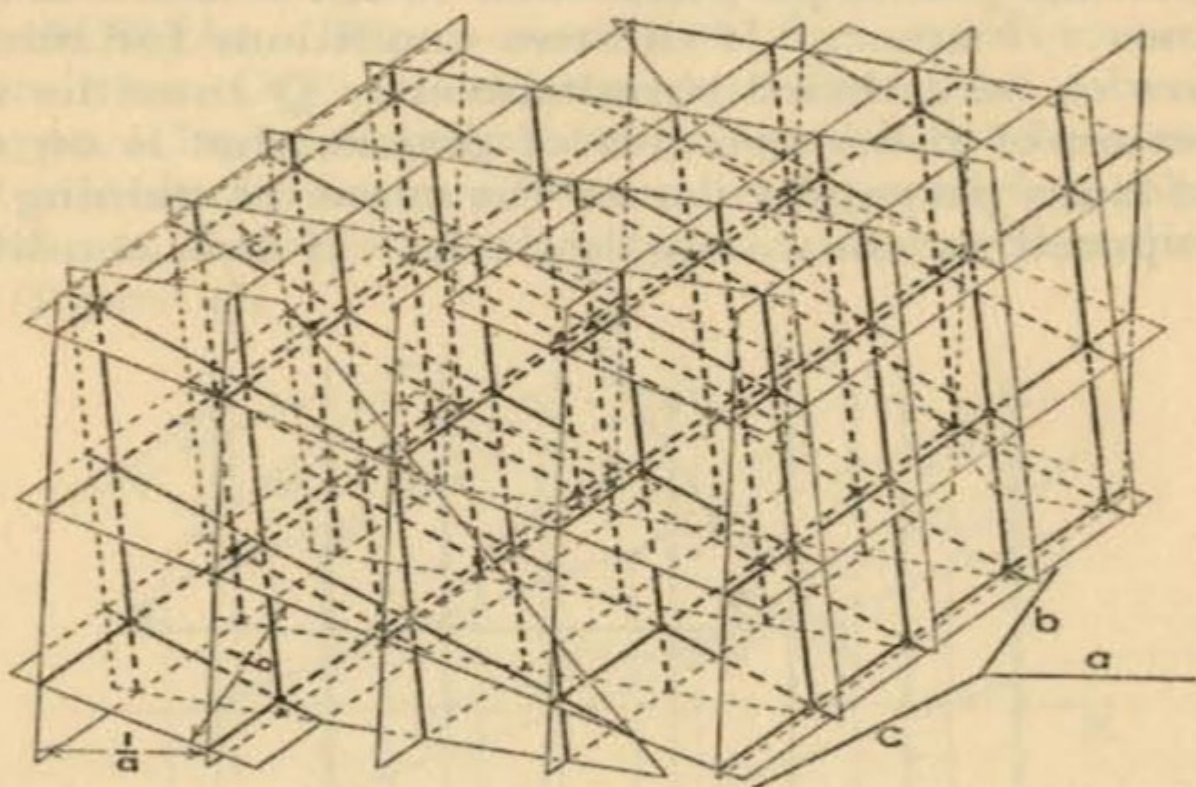


FIG. 6.—Formation of the reciprocal lattice, expressing the condition that the path differences between rays diffracted by all scattering centres in a crystal should be integral multiples of the wave-length.

in phase if Q coincides with one of these points. The new lattice is characterized by a new set of axes; that having the direction nearest to a is called a^* , that nearest b is called b^* , that nearest c is called c^* , and the appropriate angles are called α^* , β^* , γ^* . The crystal axes and the new axes coincide in direction only if the crystal axes are orthogonal, and their relative magnitudes are generally different.

There are, however, a number of interesting and curious relations between the lattices, which can be summarized in the word *reciprocal*, and the new lattice, representing the conditions that the diffracted intensity should have a maximum, is usually called the reciprocal lattice.

5. The geometrical conditions for strong diffraction are summed up in the integers h, k, l , generally called the 'indices of reflection', which specify the point of the reciprocal lattice with which Q coincides. It is convenient to call the direction of the line OQ joining the origin of the reciprocal lattice to the point h, k, l the ' hkl direction'. The angle between the incident and the diffracted rays depends only on the length S of OQ , for in the triangle OPQ , the angle OPQ is the angle of deviation, and if this is called 2θ ,

$$\begin{aligned} S = OQ &= OP \sin \theta + PQ \sin \theta \\ &= 2 \sin \theta / \lambda, \\ \lambda &= (2/S) \sin \theta. \end{aligned}$$

If $1/S$ is replaced by d/n , this is of the same form as Bragg's law. The distance OQ should therefore be the reciprocal of some interplanar spacing in the crystal lattice.

This, or at any rate the converse of it, that for every set of planes with spacing d there are points of the reciprocal lattice at distances $1/d, 2/d, 3/d, \dots$ from the origin, is easy to show. In constructing the reciprocal lattice we considered three non-parallel lines of scattering centres, which for simplicity we chose parallel to the crystal axes. If we choose them with other directions, the reciprocal lattice resulting must be the same, as it expresses the geometrical conditions necessary for the reinforcement of the scattered rays, and the final edifice must be the same, whatever the scaffolding used in constructing it. Suppose then that we take the first two lines of scattering centres lying in one of the planes of the set of spacing d , and take the third line FG so that one scattering centre belongs to each plane

of the set (figure 7). Let the spacing of the centres in this line be d' . The condition for reflection from the

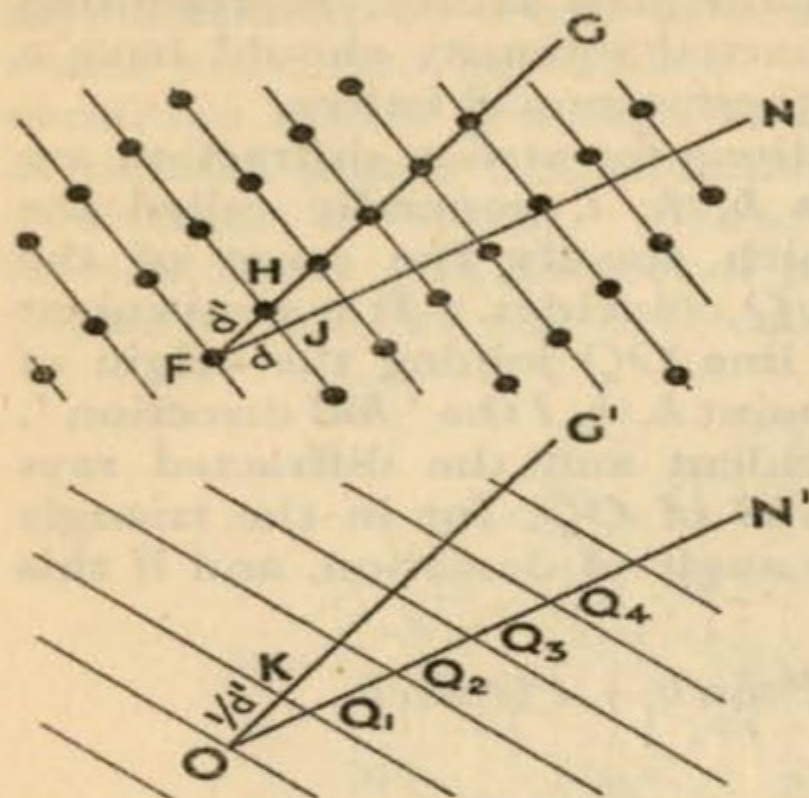


FIG. 7.—Construction to show that the reciprocal-lattice representation includes Bragg's law.

of the planes is $1/d'$. The triangles FJH and OKQ_1 are similar, since their angles are equal, so

$$d : d' :: 1/d' : OQ_1,$$

or

$$OQ_1 = 1/d.$$

The distances of the points Q_1, Q_2, \dots from O are therefore $1/d, 2/d, \dots$, so that there are points of the reciprocal lattice at these distances from the origin. These points correspond to the first, second, third, \dots orders of reflection from the planes of spacing d , but the tendency nowadays is to count only first-order reflections, and regard the higher orders as being due to different sets of planes, with spacings $d/2, d/3, \dots$, which happen to be parallel to the set with spacing d . Thus for every set of parallel planes in a crystal, there is one point of the reciprocal lattice whose distance from the

plane as from a mirror is that Q should lie on a line ON' through the origin of reciprocal space perpendicular to the plane, and the condition for reinforcement of reflections from successive planes is that Q should lie on one of a set of parallel planes perpendicular to the line of scattering centres and at a distance $1/d'$ apart. Thus Q must be one of the points Q_1, Q_2, Q_3, \dots shown in the lower part of figure 7, where ON' is parallel to FN , OG' to FG , and the spacing

origin is the reciprocal of the spacing of the planes, and the line joining the point to the origin of the reciprocal lattice (the hkl direction as defined above) is perpendicular to the planes. The planes are denoted by the same triplet of numbers that describes the point of the reciprocal lattice, and it can be shown that this triplet is the same as the Miller indices of the plane with the order of reflection included (James, pp. 5, 51).

6. The geometrical construction of paragraph 4 determines the reciprocal lattice, but for calculations it is convenient to have

the reciprocal axes a^* , b^* , c^* and angles α^* , β^* , γ^* given explicitly in terms of the crystal axes a , b , c and angles α , β , γ .

The relations between the unit cells of the lattices is shown in figure 8. Because

of the method of construction of the reciprocal lattice a^* is perpendicu-

lar to b and c , b^* to c and a , and c^* to a and b . The reciprocal relations follow: a is perpendicular to b^* and c^* , b to c^* and a^* , and c to a^* and b^* . Also because of the method of construction, the projection of a^* on a is of length $1/a$, that of b^* on b is of length $1/b$, and of c^* on c is of length $1/c$. The reciprocal relations follow; if the angle between a and a^* is ψ , the projection of a^* on a is $a^* \cos \psi$, so $a^* \cos \psi = 1/a$, $\cos \psi = 1/aa^*$, and the projection of a on a^* is $a \cos \psi = a/aa^* = 1/a^*$. Similarly the projection of b on b^* is $1/b^*$, and of c on c^* is $1/c^*$.

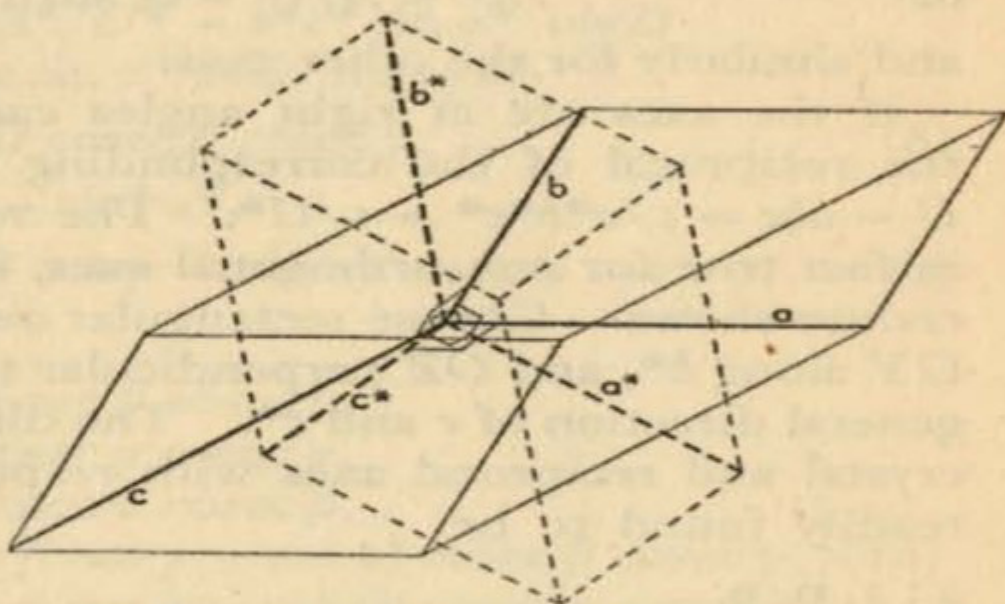


FIG. 8.—Relations between the axes of the crystal lattice and those of the reciprocal lattice. Right angles are marked.

From these relations it is easy to find the lengths of the reciprocal axes. Let the area of the face of the parallelepiped bounded by b and c be A , that of the face bounded by c and a be B , that of the face bounded by a and b be C , the volume of the parallelepiped be U , and let the corresponding functions of the reciprocal axes be denoted by the same letters starred. The volume U is equal to the area of the face A multiplied by the perpendicular distance to the opposite face, and this distance is the projection of a on a^* , since a^* is perpendicular to A . Thus $A(1/a^*) = U$, or

$$a^* = A/U = bc \sin \alpha / U, \quad (1)$$

and similarly for the other axes.

If the axes are at right angles each reciprocal axis is the reciprocal of the corresponding crystal axis, so that $U = abc = 1/a^*b^*c^* = 1/U^*$. The relation $U = 1/U^*$ is in fact true for non-orthogonal axes, as the following procedure shows. Choose rectangular axes with OX along a , OY along b^* , and OZ perpendicular to these and with the general direction of c and c^* . The direction cosines of the crystal and reciprocal axes with respect to these axes are readily found to be

$$\left. \begin{aligned} a &: 1, 0, 0, \\ b &: \cos \gamma, D \operatorname{cosec} \beta, (\cos \alpha - \cos \beta \cos \gamma) \operatorname{cosec} \beta, \\ c &: \cos \beta, 0, \sin \beta, \\ a^* &: D \operatorname{cosec} \alpha, (\cos \alpha \cos \beta - \cos \gamma) \operatorname{cosec} \alpha \operatorname{cosec} \beta, \\ &\quad - D \operatorname{cosec} \alpha \cot \beta, \\ b^* &: 0, 1, 0, \\ c^* &: 0, (\cos \beta \cos \gamma - \cos \alpha) \operatorname{cosec} \beta \operatorname{cosec} \gamma, \\ &\quad D \operatorname{cosec} \beta \operatorname{cosec} \gamma, \end{aligned} \right\} \quad (2)$$

where

$$D = \sqrt{(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)}. \quad (3)$$

Some of these direction cosines can be written down immediately, and the rest follow from known angular relations between the axes. The volume of a parallelepiped is equal to the product of its edges multiplied by the determinant of their direction cosines, so

$$U = abcD, \quad (4)$$

and
$$U^* = a^*b^*c^*D^2 \operatorname{cosec} \alpha \operatorname{cosec} \beta \operatorname{cosec} \gamma. \quad (5)$$

Replacing a^* by $bc \sin \alpha / U$, and so on, gives

$$U^* = a^2b^2c^2D^2/U^3 = 1/U, \quad (6)$$

as it was required to show. Use of this result gives

$$\left. \begin{aligned} a^* &= A/U = \sin \alpha / aD, \\ b^* &= B/U = \sin \beta / bD, \\ c^* &= C/U = \sin \gamma / cD. \end{aligned} \right\} \quad (7)$$

From the relation reciprocal to equation 1

$$\begin{aligned} a &= A^*/U^* = b^*c^* \sin \alpha^* \cdot abcD \\ &= a \sin \alpha^* \sin \beta \sin \gamma / D, \end{aligned}$$

$$\sin \alpha^* = D \operatorname{cosec} \beta \operatorname{cosec} \gamma, \quad (8)$$

or, since $\cos^2 \alpha^* = 1 - \sin^2 \alpha^*$,

$$\cos \alpha^* = (\cos \beta \cos \gamma - \cos \alpha) \operatorname{cosec} \beta \operatorname{cosec} \gamma, \quad (9)$$

so that

$$\left. \begin{aligned} \sin \alpha^* &= D \operatorname{cosec} \beta \operatorname{cosec} \gamma, \\ \sin \beta^* &= D \operatorname{cosec} \gamma \operatorname{cosec} \alpha, \\ \sin \gamma^* &= D \operatorname{cosec} \alpha \operatorname{cosec} \beta, \\ \cos \alpha^* &= (\cos \beta \cos \gamma - \cos \alpha) \operatorname{cosec} \beta \operatorname{cosec} \gamma, \\ \cos \beta^* &= (\cos \gamma \cos \alpha - \cos \beta) \operatorname{cosec} \gamma \operatorname{cosec} \alpha, \\ \cos \gamma^* &= (\cos \alpha \cos \beta - \cos \gamma) \operatorname{cosec} \alpha \operatorname{cosec} \beta. \end{aligned} \right\} \quad (10)$$

7. These results make it possible to write down the general expression for the Bragg angle in terms of the indices hkl . The length S of the line joining the point hkl to the origin of the reciprocal lattice may be obtained in the following way. Its components along the reciprocal axes are ha^* , kb^* , lc^* ; let it make angles λ , μ , ν with these axes. The projection of S on any axis is equal to the sum of the projections of its components, so

$$S \cos \lambda = ha^* + kb^* \cos \gamma^* + lc^* \cos \beta^*, \quad (11)$$

$$S \cos \mu = ha^* \cos \gamma^* + kb^* + lc^* \cos \alpha^*, \quad (12)$$

$$S \cos \nu = ha^* \cos \beta^* + kb^* \cos \alpha^* + lc^*, \quad (13)$$

and S is equal to the sum of the projections of its

components on itself, so

$$S = ha^* \cos \lambda + kb^* \cos \mu + lc^* \cos \nu. \quad (14)$$

Multiplying (11) by ha^* , (12) by kb^* , (13) by lc^* and adding gives

$$\begin{aligned} h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^*c^* \cos \alpha^* \\ + 2lhc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^* \\ = S(ha^* \cos \lambda + kb^* \cos \mu + lc^* \cos \nu) \\ = S^2, \end{aligned} \quad (15)$$

by equation 14. Since $S = 2 \sin \theta / \lambda$, the Bragg angle is given by

$$\begin{aligned} 4 \sin^2 \theta / \lambda^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^*c^* \cos \alpha^* \\ + 2lhc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^*. \end{aligned} \quad (16)$$

This equation may be simplified considerably for crystals not of the triclinic system. Expressions for each crystal system are given in the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, and many books on X-ray analysis. For the cubic system with $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$ it reduces to

$$S^2 = 4 \sin^2 \theta / \lambda^2 = (h^2 + k^2 + l^2) / a^2. \quad (17)$$

8. One reason for the importance of the reciprocal lattice is its close relation with X-ray diffraction photographs. X-ray photographs resemble the reciprocal lattice much more than they resemble the crystal lattice; one could perhaps say that the photograph is merely a more or less distorted reciprocal lattice. For special purposes cameras have been designed that reproduce a section of the reciprocal lattice with little or no distortion (Buerger, 1944). In general, however, the distortion is more or less severe, and before proceeding with the development of the reciprocal lattice it may be well to describe briefly certain types of X-ray camera and the photographs they produce.

9. In the simplest possible arrangement the crystal and the film are both stationary and a narrow beam of practically parallel X-rays falls on the crystal. If the beam contains a wide range of wave-lengths this gives a so-called Laue

photograph (James, p. 19), which is not nowadays of primary importance. If the beam is monochromatic and the crystal perfect there will be in general no strong diffraction maxima. The reciprocal lattice and the line OP (paragraph 3) are fixed, and strong diffraction would occur only if some point of the reciprocal lattice were at a distance $1/\lambda$ from P , or in other words were to lie on a sphere (called the 'sphere of reflection') with centre at P and passing through the origin of the reciprocal lattice. For an arbitrary orientation of the crystal this is an unlikely coincidence. If the crystal is not perfect, however, the region of appreciable scattering is not concentrated in a point of the reciprocal lattice, but extends to a greater or less distance from it, and it is quite likely that the sphere of reflection will intersect one or more scattering regions, and give rise to more or less diffuse streaks or spots on the photograph. Cameras specially designed for investigating such diffuse regions in reciprocal space are now in use, embodying ingenious devices for obtaining a beam as nearly monochromatic as possible. Any continuous radiation would produce Laue spots and make the interpretation more difficult.

10. If the crystal is oscillated or rotated while the exposure is being made the reciprocal lattice will oscillate or rotate through the same angle, many points of the reciprocal lattice will pass in turn through the sphere of reflection, and the strong scattering occurring as each point intersects the sphere will produce corresponding points on the film. In the commonest type of moving-crystal camera the crystal is mounted in the centre of a cylindrical * film, adjusted so that one axis is vertical, and rotated about this axis during exposure to a horizontal beam of X-rays. An oscillation with uniform angular velocity over a convenient range (5° , 10° or 15°) may be substituted for a complete rotation. Suppose for definiteness that the c axis is vertical.

* A flat film may be used, but the 'layer-lines' are then curved (James, pp. 24-7).

Then the plane of the reciprocal lattice containing a^* and b^* (the plane $l = 0$) is horizontal, and OP lies in it (figure 9).

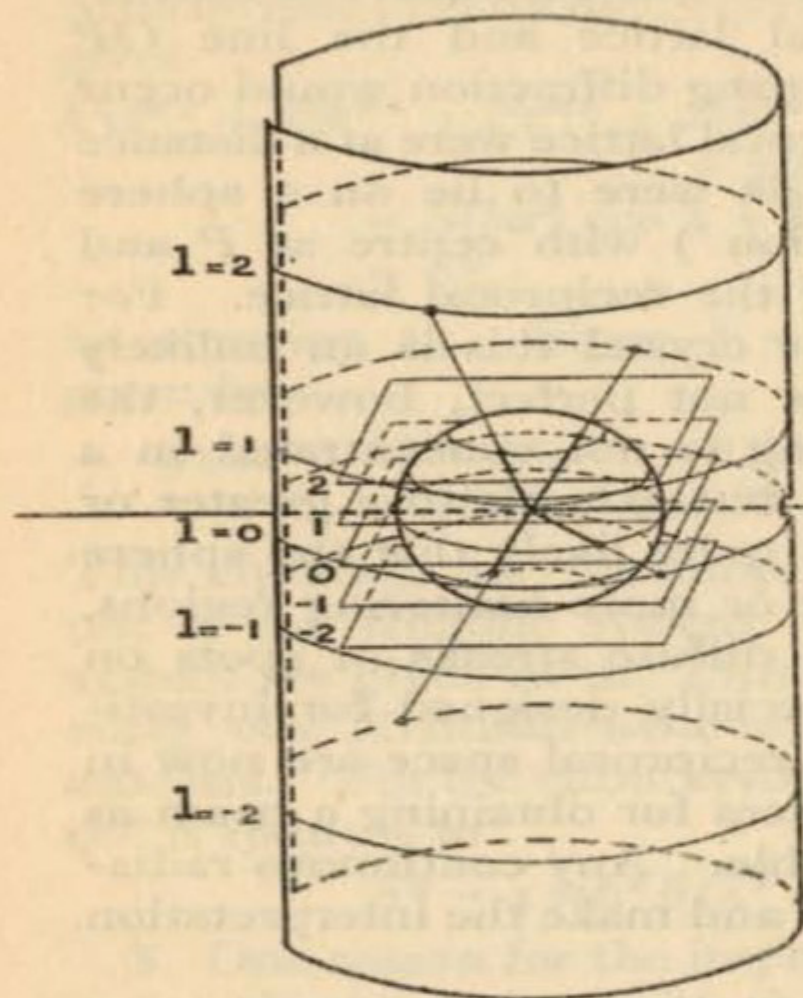


FIG. 9.—Formation of layer lines on a moving-crystal photograph. The X-rays emerge from the sphere of reflection at O , P is the centre of the sphere, and four possible positions of Q are shown, leading to spots with $l = 2, 1, 0$ and -2 . As the crystal moves the reciprocal lattice rotates with it, bringing other points to the surface of the sphere of reflection, and producing other spots on the layer lines.

The sphere of reflection cuts it in a great circle, and cuts the parallel planes for which $l = \pm 1, \pm 2, \dots$ in circles of progressively diminishing size. The diffracted rays for $l = 0$ all lie in a horizontal plane, and strike the film along the 'equator'. The

diffracted rays for other values of l lie on right circular cones whose angle depends on the values of l and c ; the semi-angle is easily seen to be $\arccos(l\lambda/c)$. These cones intersect the film in circles whose planes are parallel to the equatorial plane, so that when the film is opened out the diffraction spots lie on a series of parallel 'layer lines'. The length of the c axis is readily obtained from the spacing of these lines and the radius of the camera. The l index of a spot is equal to the number, counted from the equator as zero, of the line on which it lies. The

other indices of the spots are generally obtained by a method described by Bernal (1926) which involves a

certain amount of trial and error, but a direct method has been devised (Bunn, Peiser and Turner-Jones 1944; Turner-Jones and Bunn 1946).

11. In the Weissenberg camera a cylindrical screen is placed between the crystal and the film, with a slot placed so as to allow only the spots of one layer line to pass through. The film is moved parallel to its axis as the crystal is rotated, so that the spots are all over the film, instead of being concentrated on a line. It can be shown that they lie on two families of curves, from which the pair of indices not determined by the layer line can be found directly. The method is used chiefly in structure determinations, and will not be further described here (Weissenberg, 1924).

12. The methods mentioned so far require a fairly large crystal (say not less than 0.01 cm. in linear dimensions), and if this is not available the powder method can be used. In this the specimen, consisting of a large number of small crystals of random orientation, is placed in the centre of a cylindrical film and bathed in a narrow beam of approximately parallel X-rays. During exposure the specimen is rotated to make the orientation still more random. By this means nearly all directional effects are averaged out, the angle of deviation being the only remaining variable. The intensity of the X-rays falling on the film with a deviation between 2θ and $2(\theta + d\theta)$ will depend on all the intensity that, in the representation in reciprocal space, lies between spheres of radii $S = 2 \sin \theta / \lambda$ and

$$S + dS = 2 \sin \theta / \lambda + d(2 \sin \theta / \lambda).$$

If $I(\theta) d\theta$ is the intensity diffracted with a Bragg angle between θ and $\theta + d\theta$, and $I(S) dS$ is the intensity between concentric spheres with radii S and $S + dS$, then except for certain geometrical factors,

$$\begin{aligned} I(\theta) d\theta &= I(S) dS \\ &= (2 \cos \theta / \lambda) I(S) d\theta, \end{aligned}$$

so that

$$I(\theta) = (2 \cos \theta / \lambda) I(S). \quad . \quad . \quad (18)$$

In favourable cases the spheres will not intersect more than two regions of high intensity in reciprocal space (say those near h, k, l and near $-h, -k, -l$), and the photographs will consist of a series of lines. Usually the regions round h, k, l and round $-h, -k, -l$ are related by a centre of symmetry, and their superposition on the film causes no trouble. In unfavourable cases the spheres will intersect regions corresponding to several values of h, k, l and the interpretation of the film becomes more complicated, but powder photographs are of some use as long as discrete lines are visible, even when the lines are due to the superposition of several regions of high intensity.

For purposes of structure analysis the important quantity connected with a line is its total intensity, that is $I = \int I(\theta) d\theta$, the integral being taken over a sufficient length of film to include the whole line. Except for certain geometrical factors, this is the intensity that would be scattered by one unit cell at the angle θ multiplied by the number of unit cells in the specimen. We shall be more concerned with the shape of the line, $I(\theta)$, and especially with its breadth, or the range of angle over which the reflection extends. Various definitions of this have been used, the earliest being the half breadth. If I_0 is the maximum value of $I(\theta)$, and θ_1, θ_2 are the values of θ for which $I(\theta) = \frac{1}{2}I_0$, the half breadth is defined as

$$\beta' = 2(\theta_2 - \theta_1). \quad (19)$$

A definition of breadth better adapted to calculation is the integral breadth, defined by

$$\beta = 2I/I_0. \quad (20)$$

(The factor 2 occurs in these expressions because they were originally defined in terms of the angle of deviation, not the Bragg angle.) If I_s is the maximum value of $I(S)$,

$$\beta = I\lambda/I_s \cos \theta, \quad (21)$$

so that the apparent particle size is

$$\varepsilon = \lambda/\beta \cos \theta = I_s/I. \quad (22)$$

13. In deriving the relation between $I(\theta)$ and $I(S)$ above it was tacitly assumed that the variation of intensity on the film depended only on the distribution of intensity in reciprocal space. This is never true in practice; the lack of parallelism in the incident beam, the finite length and diameter of the specimen, and the range of wave-length included in even a crystal-reflected X-ray beam would lead to a line of finite breadth even if the specimen were ideal. The line profile obtained by photometering the film differs from that which the crystal imperfection alone would produce, and it is necessary to correct it before using it to obtain information about the specimen. Several methods have been devised for doing this, depending on the use of two lines, one produced by the specimen under investigation, and the other produced under the same experimental conditions by a specimen as nearly ideal as possible. From the two line profiles it is possible to derive the line profile due to specimen imperfection alone, but the process is tedious and one has generally to be content with the integral breadth only. It is found that the breadth of a line produced by a specimen with imperfections is not simply the sum of the breadth due to experimental conditions and the breadth due to specimen imperfection. The squares of the breadths are more nearly additive, but the exact relation depends on the type of imperfection and the experimental arrangement. For routine work the correction procedure devised by Jones (1938) is perhaps the best.

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CHAPTER III

RECIPROCAL SPACE FOR SMALL CRYSTALS

1. As was seen in the preceding chapter, the radiation diffracted by a crystal is at a maximum when the relation between the directions of the incident and diffracted rays is such that the point Q , found by drawing a line OP of length $1/\lambda$ from the origin of the reciprocal lattice parallel to the incident ray reversed, and a line PQ from its terminus parallel to the diffracted ray, coincides with one of the points of the reciprocal lattice. If the coincidence is not exact there is still some diffracted radiation, and the next step in the investigation is to find the way in which the intensity of the diffracted radiation depends on the position of Q . Suppose that Q is nearly at the point h, k, l of the reciprocal lattice, its co-ordinates in terms of the reciprocal axes being $h + u, k + v, l + w$. The successive scattering centres in the line OX of figure 2, chapter II, will no longer be scattering exactly in phase, and the bigger u is, that is the further Q departs from the plane for which $B'D + B'E = h\lambda$, the greater will be the phase difference between the rays scattered by successive centres. If u were equal to unity, Q would lie on the plane corresponding to $h + 1$, and the phase difference would be one wavelength, or 2π radians. For smaller values of u the phase difference between rays scattered by successive centres will be proportionately less, and so equal to $2\pi u$ radians. If the length of the line of centres is T the number of them is T/a , and the amplitude of the scattered radiation is the resultant of $N \equiv T/a$ equal vibrations each $\delta \equiv 2\pi u$ radians out of phase with the preceding one.

2. A graphical method of finding the resultant G of N equal vibrations with successive phase differences δ is illustrated in figure 1. Each vibration is represented by a line of unit length, and the phase differences are represented by

drawing each line at an angle δ to the preceding one. The resultant amplitude is given by the distance between the free ends of the first and last line. In the present case N is large, and the polygon made from the individual vibrations may be considered as the arc of a circle, at any rate as long as u is small compared with unity. The angle subtended by the arc at its centre is $N\delta$, and its length is N , so the radius of the circle is $1/\delta$. The length of the secant joining its ends, which is the amplitude of the resultant, is twice the radius multiplied by the sine of half the angle subtended at the centre, or

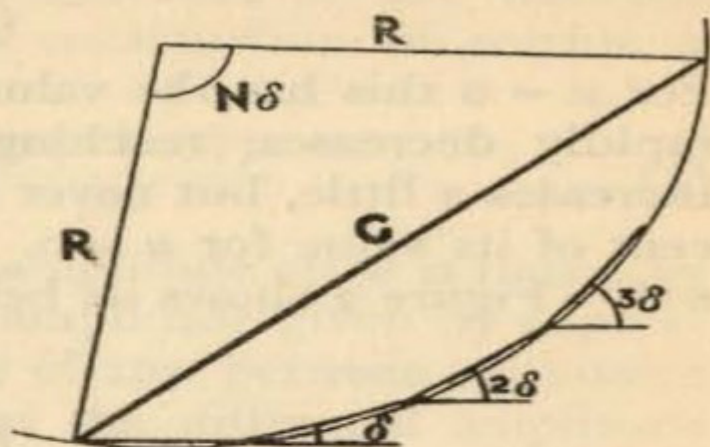


FIG. 1.—Summation of N out-of-phase vibrations.

$$\frac{2}{\delta} \sin \frac{N\delta}{2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

More accurately, the angle subtended by the arc of the circle is $N\delta$, but its length is $N \cdot 2R \arcsin(1/2R)$, where R is the radius of the circle. The radius is therefore given by

$$2NR \arcsin(1/2R) = N\delta R,$$

or

$$R = 1/2 \sin(\delta/2).$$

The exact expression for the reflected amplitude is thus

$$\frac{\sin(N\delta/2)}{\sin(\delta/2)},$$

but the expression (1) is a sufficient approximation for all applications made here.

3. On substituting the values given above for N and δ the resultant amplitude becomes

$$\frac{\sin(\pi Tu/a)}{\pi u} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

The reflected intensity is proportional to the square of this, that is to

$$\frac{\sin^2(\pi Tu/a)}{(\pi u)^2} \quad (3)$$

For $u = 0$ this has the value $(T/a)^2$, and as u increases it rapidly decreases, reaching zero for $u = a/T$. It then increases a little, but never amounts to more than five per cent of its value for $u = 0$. For large u it falls to zero as u^{-2} . Figure 2 shows its behaviour as a function of u .

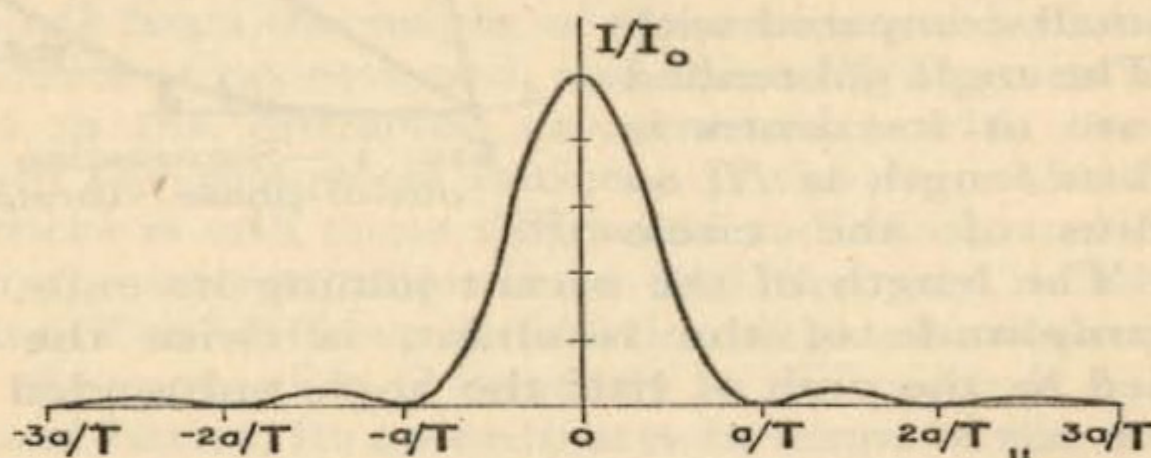


FIG. 2.—Resultant of $N = T/a$ out-of-phase vibrations as a function of u .

4. We have so far considered the behaviour of a single line of scattering centres. In order to investigate the behaviour of a complete crystal it is necessary to know its shape. In principle it is possible to work out the scattering from a crystal of any shape, and it has indeed been done for many (Patterson, 1939). To illustrate the problem two shapes will be considered here, the parallelepiped and the sphere. Others can be worked out on the same principles, but the mathematics becomes complicated. The general expression is derived in section 6 below.

Suppose, then, that the crystal has the form of a parallelepiped, whose edges are parallel to the crystal axes, and are of lengths X , Y , Z . The value of T for all lines of scattering centres parallel to the a -axis will be X , and the dependence of the amplitude of reflection on u will be

$$\frac{\sin(\pi Xu/a)}{\pi u} \quad (4)$$

for each such line. The dependence of the amplitude on v is found by adding Y/b vibrations, each of amplitude $\sin(\pi Xu/a)/\pi u$, with a phase difference of $2\pi v$ between successive vibrations. By the construction of section 2 the resultant is

$$\frac{\sin(\pi Xu/a)}{\pi u} \frac{\sin(\pi Yv/b)}{\pi v} \quad (5)$$

Finally, the dependence of the amplitude on w is found by adding Z/c vibrations, each of amplitude given by expression (5), with a phase difference of $2\pi w$ between successive vibrations. The dependence of the diffracted amplitude G on u, v, w is therefore

$$G(u, v, w) = \frac{\sin(\pi Xu/a)}{\pi u} \frac{\sin(\pi Yv/b)}{\pi v} \frac{\sin(\pi Zw/c)}{\pi w} \quad (6)$$

The diffracted intensity as a function of position in reciprocal space, $H(u, v, w)$, is proportional to the square of this, that is

$$H(u, v, w) = \frac{\sin^2(\pi Xu/a)}{(\pi u)^2} \frac{\sin^2(\pi Yv/b)}{(\pi v)^2} \frac{\sin^2(\pi Zw/c)}{(\pi w)^2} \quad (7)$$

The maximum value of $H(u, v, w)$, for $u = v = w = 0$, is $(XYZ)^2/(abc)^2$. Since XYZ is proportional to the volume V of the crystal, and abc to the volume U of the unit cell, the maximum value of H is the square of the total number of unit cells in the crystal. For a given distance from the point of the reciprocal lattice H has its greatest values along the reciprocal axes, that is, the intensity falls off least rapidly in directions perpendicular to the faces of the crystal. This is found to be true in general; each plane face of a crystal is represented by a 'spike' of increased intensity in reciprocal space, the direction of the spike being perpendicular to the face (von Laue, 1936; Ewald, 1938, 1940). If the crystal is plate-like, with, say, X and Y much greater than Z , the intensity of reflection as a function of position in reciprocal space is practically concentrated on the c^* -axis, forming a line perpendicular

to the plate and of length inversely proportional to its thickness. If the crystal is needle-like, with, say, X and Y very much less than Z , the intensity of reflection is concentrated into a plate perpendicular to c^* , extending a little bit further in the directions of a^* and b^* than in the

intermediate directions. These plate-needle and needle-plate relations are a further illustration of the reciprocal nature of the relations between the two sets of axes.

5. For a spherical crystal the calculation is a little more complex, and to simplify it as far as possible it will be

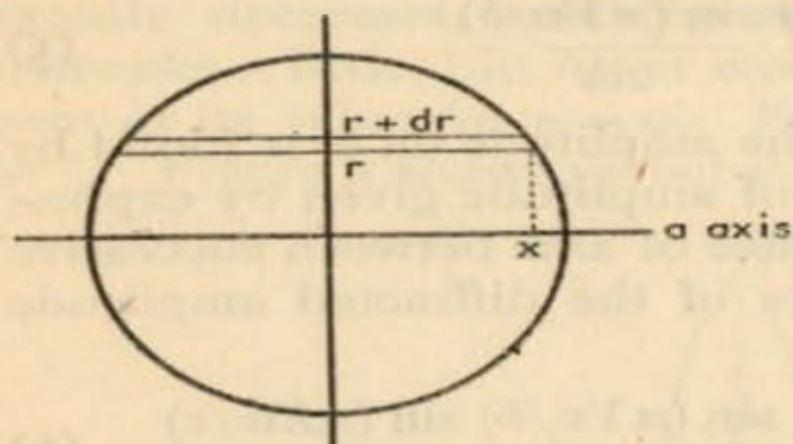


FIG. 3.—Calculation of the intensity of reflection from a spherical crystal.

assumed that the axes of the crystal are orthogonal. Suppose that the diameter of the sphere is D . The length of a line of scattering centres at a distance $r = \sqrt{(D/2)^2 - x^2}$ from the a -axis is $2x$ (figure 3), so the amplitude diffracted by this line is, as a function of u ,

$$\frac{\sin(2\pi xu/a)}{\pi u} \quad . \quad . \quad . \quad . \quad (8)$$

The amplitude diffracted by the whole crystal, for $v = w = 0$, is got by summing this expression for all lines of scattering centres. The number of lines of scattering centres passing through unit area perpendicular to a is equal to a/U , so that the sum is approximately

$$\begin{aligned} G &= \int_{D/2}^0 \frac{\sin(2\pi xu/a)}{\pi u} \frac{a}{U} 2\pi r dr \\ &= (2a/uU) \int_{D/2}^0 \sin(2\pi xu/a) \sqrt{(D/2)^2 - x^2} d\sqrt{(D/2)^2 - x^2} \\ &= (2a/uU) \int_0^{D/2} x \sin(2\pi xu/a) dx. \quad . \quad . \quad . \quad (9) \end{aligned}$$

The integration is easily performed by parts, and gives as the amplitude of the diffracted radiation

$$G(u) = \frac{\pi}{2U} \frac{\sin(\pi Du/a) - (\pi Du/a) \cos(\pi Du/a)}{(\pi u/a)^3}. \quad (10)$$

This has been derived as the amplitude diffracted as a function of u for $v = w = 0$. For a spherical crystal, however, there is nothing special about the a -axis, and the amplitude of the diffracted radiation will depend only on the distance $s = u/a$ of Q from the point of the reciprocal lattice. This amplitude $G(s)$ will therefore be given by equation (10) with u/a replaced by s . The maximum value of G , being the limit of equation (10) for $u = 0$, is $\pi D^3/6U$, which is, as would be expected, just the total number of unit cells in the crystal. At the points of the reciprocal lattice all unit cells scatter in phase, whatever the crystal shape, and the intensity of reflection is proportional to the square of the number of unit cells. The total intensity of a reflection (that is, the integral of the intensity over all the region of reciprocal space for which the intensity is appreciable) is proportional to the actual number of unit cells, so the 'integral breadth' in reciprocal space of a reflection is $N/N^2 = 1/N$, whatever the crystal shape. The *shapes* of the regions of high intensity, and hence the details of the X-ray photographs, are of course dependent on the crystal shape.

6. Though it is not needed for applications in future chapters it is perhaps worth while to write down the general expression for the amplitude of reflection as a function of position in reciprocal space. For simplicity the treatment will be limited to orthogonal axes. The rays scattered by the unit cell that is n_1 unit cells in the a direction, n_2 in the b direction, and n_3 in the c direction away from the cell at the centre of gravity of the crystal will be advanced in phase with respect to those scattered by the cell at the centre of gravity by

$$\delta_n = 2\pi(n_1u + n_2v + n_3w) \quad . \quad . \quad (11)$$

radians. The amplitude scattered by the whole crystal will be the sum of $N \equiv V/U$ contributions (where V is the volume of the crystal and U the volume of a unit cell) of equal magnitudes, and phases given by equation (11).

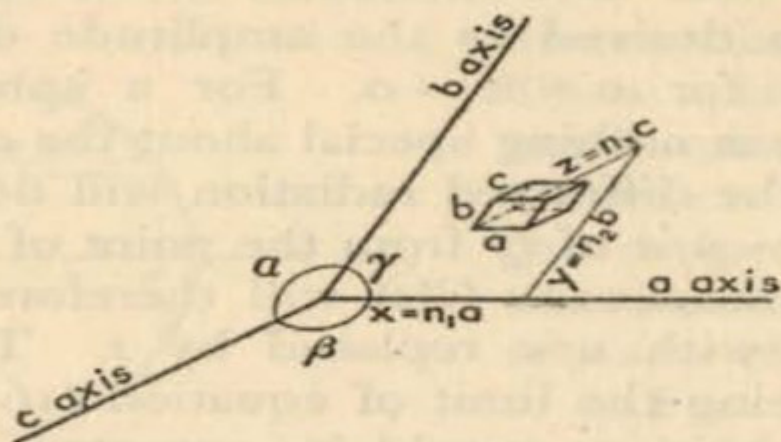


FIG. 4.—Position of the n^{th} unit cell.

These cannot be added by the construction given in paragraph 2, since δ_n depends on three variables, n_1, n_2, n_3 , but the addition can be done trigonometrically by noting that the resultant of a number of lines of lengths F_1, F_2, \dots at angles of $\delta_1, \delta_2, \dots$ with the horizontal is represented in magnitude G by

$$G^2 = A^2 + B^2 \quad . \quad . \quad . \quad (12)$$

and in phase δ by

$$\tan \delta = B/A, \quad . \quad . \quad . \quad (13)$$

where

$$A = F_1 \cos \delta_1 + F_2 \cos \delta_2 + \dots \quad (14)$$

and

$$B = F_1 \sin \delta_1 + F_2 \sin \delta_2 + \dots$$

In the present case the lengths are all unity, and the phases are given by equation (11), so

A = the sum of $\cos 2\pi(n_1u + n_2v + n_3w)$ for all values of n_1, n_2, n_3 ,

and B = the sum of $\sin 2\pi(n_1u + n_2v + n_3w)$ for all values of n_1, n_2, n_3 .

If the crystal is reasonably large u, v, w are small compared with unity, and the summation may be replaced by integration without appreciable error. The number of unit cells

in the volume element $dx dy dz$ is $dx dy dz/U$, and $x = n_1a$, $y = n_2b$, $z = n_3c$, so

$$A = U^{-1} \iiint \cos 2\pi(ux/a + vy/b + wz/c) dx dy dz, \quad (15)$$

$$B = U^{-1} \iiint \sin 2\pi(ux/a + vy/b + wz/c) dx dy dz, \quad (16)$$

$$H(u, v, w) = A^2 + B^2, \quad (17)$$

where the integrations extend throughout the volume of the crystal. If the shape of the crystal has a centre of

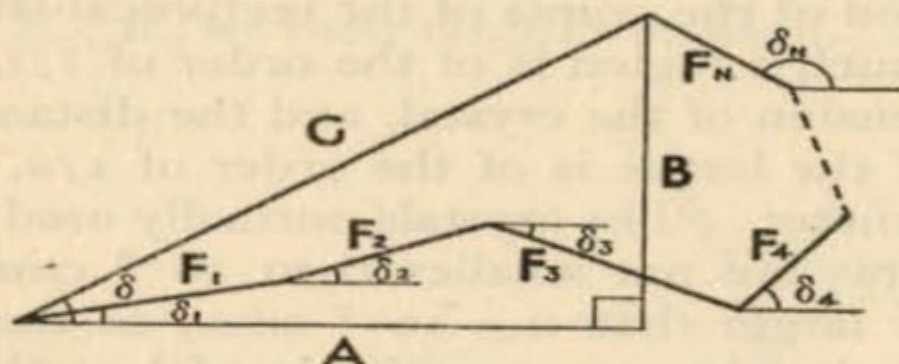


FIG. 5.—Summation of the contributions from N unit cells.

symmetry B vanishes. It will be noticed that if u, v, w are replaced by $-u, -v, -w$, A is unaffected and B is merely changed in sign. $H(u, v, w)$ has therefore a centre of symmetry at the point of the reciprocal lattice, even if the crystal shape is not centrosymmetric. The mathematically-inclined reader may verify that equations (15)–(17) lead to (8) and (10) for crystals having the shapes of a parallelepiped and sphere respectively.

7. It will be noticed that none of the expressions giving the amplitude or intensity as a function of u, v, w depends explicitly on h, k, l . The surroundings of each point of the reciprocal lattice are therefore identical, except perhaps for a factor depending on the 'structure amplitude'. This should be noted, as it contrasts with the appearance of the reciprocal lattice when the crystal is distorted or contains 'mistakes'.

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CHAPTER IV

POWDER PHOTOGRAPHS OF SMALL CRYSTALS

1. It has been seen that X-ray diffraction is concentrated into small regions of reciprocal space in the immediate neighbourhood of the points of the reciprocal lattice. The diameter of such a region is of the order of $1/t$, where t is a linear dimension of the crystal, and the distance between the points of the lattice is of the order of $1/a$, where a is a lattice parameter. The crystals normally used in moving-crystal cameras are not smaller than 10^{-2} cms., and a is not normally larger than 2×10^{-7} cms., so the regions of strong diffraction have a magnitude of less than 10^{-4} of their distance apart. The region of strong diffraction is therefore inappreciably small, and the finite size of the spots on rotating-crystal photographs is not due to diffraction in the ordinary use of the word. Geometrical optics suffices to explain the size and shape of the spots. With powder photographs, however, there is no lower limit to the size of crystals that may be used, and if t is of the order of 10^{-5} cms. the size of the regions of large intensity becomes appreciable in comparison with their distance apart, and the lines on the powder pattern are broadened. It is necessary therefore to determine how the broadening depends on the size and shape of the crystals producing the powder pattern.

2. The intensity diffracted with a Bragg angle between θ and $\theta + d\theta$ on a powder photograph is proportional to the intensity that, in the representation in reciprocal space, lies between concentric spheres of radii $S = 2 \sin \theta / \lambda$ and $S + dS = 2 \sin \theta / \lambda + (2 \cos \theta / \lambda) d\theta$, and the relation between the line-profile $I(\theta) d\theta$ and the total intensity included between the spheres $I(S) dS$ is (chapter II, paragraph 12)

$$I(\theta) = (2 \cos \theta / \lambda) I(S). \quad . \quad . \quad (1)$$

The line-profile on the powder photograph can be got therefore if the integral of $H(u, v, w)$ over the space between the spheres can be determined. With expressions for H as complicated as equation (7) or the square of equation (10) of chapter III this is difficult, but it has been done for the second one (Patterson, 1939). Normally, however, S is very large compared with the regions over which H is appreciable, and no error is introduced by replacing the spheres K_1, K_2 by their tangent planes L_1, L_2 (figure 1).

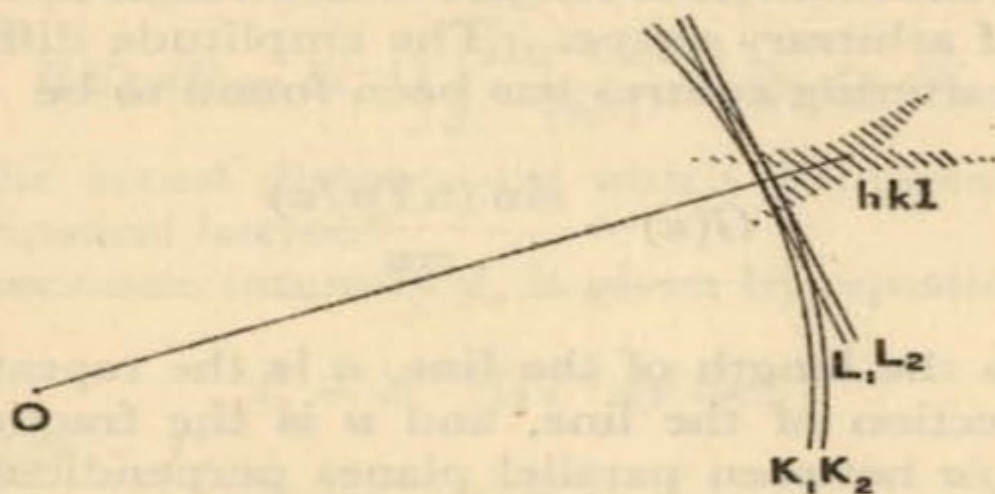


FIG. 1.—Determination of the intensity of reflection as a function of θ from the intensity as a function of position in reciprocal space.

The integral over the region between the planes is difficult enough, and is in fact practicable only if the crystals are spherical, or for certain reflections from a parallelepiped. For spherical crystals it has been done by Patterson (1939), and attempts for other crystal shapes have been made by replacing the correct expressions for H by approximate ones that are easier to integrate (von Laue, 1936; Jones, 1938; etc.). This procedure is, however, of doubtful validity, and gives results that are correct only in order of magnitude.

The direct calculation for spherical crystals is somewhat too complex to reproduce here, but it gives the same result as we shall obtain by a simpler method. Instead of calculating the amplitude of reflection from the whole crystal

as a function of position in reciprocal space, squaring to get the intensity, and integrating to get the intensity with S between S and $S + dS$, we shall take the intensity that is scattered with S between S and $S + dS$ by a single line of scattering centres in the crystal, and sum it for all parallel lines. It is obvious that the second process contains fewer mathematical steps, and it happens in addition that they are easier to carry out.

3. The problem is to calculate the integral breadth of a general reflection (that is, one with indices h, k, l) from a crystal of arbitrary shape. The amplitude diffracted by a line of scattering centres has been found to be

$$G(u) = \frac{\sin(\pi Tu/a)}{\pi u}, \quad (2)$$

where T is the length of the line, a is the repeat distance in the direction of the line, and u is the fraction of the distance $1/a$ between parallel planes perpendicular to the line by which Q misses the nearest point of the reciprocal lattice. The intensity scattered with u between u and $u + du$ is then

$$H(u) du = \frac{\sin^2(\pi Tu/a)}{(\pi u)^2} du. \quad (3)$$

Suppose that the line of scattering centres is parallel to the line joining the origin of the reciprocal lattice to the point h, k, l , and that x, y, z are orthogonal axes in the crystal with x in the direction of the line. The total intensity scattered by the crystal with u between u and $u + du$ will be got by summing expressions like equation (3) for all such lines of scattering centres in the crystal, or to a sufficient approximation by multiplying (3) by the number of lines per unit area and integrating with respect to y and z throughout the crystal. The number of lines of scattering centres passing through unit area perpendicular

to the lines is a/U , where U is the volume of the unit cell, so

$$I(u) du = \frac{a}{U} \iiint \frac{\sin^2 (\pi T u / a)}{(\pi u)^2} dy dz du. \quad (4)$$

This quantity $I(u)$ is very closely related to $I(S)$; in fact, the only difference is that u is expressed as a fraction of the distance $1/a$ between parallel planes, and S is an actual distance in reciprocal space. By replacement of du by $a dS$ and u/a by s equation (4) becomes

$$I(S) dS = U^{-1} \iiint \frac{\sin^2 (\pi T s)}{(\pi s)^2} dy dz dS, \quad (5)$$

s being the actual distance by which S misses the point of the reciprocal lattice.*

The maximum intensity I_s is given by equation (5) with $s = 0$, so

$$I_s = U^{-1} \iiint T^2 dy dz, \quad (6)$$

or, since $\int dx = T$,

$$\begin{aligned} I_s &= U^{-1} \iiint T dx dy dz \\ &= U^{-1} \int_V T dV, \end{aligned} \quad (7)$$

where the integration extends throughout the volume of the crystal. The total intensity I of a reflection is equal to the number of unit cells in the crystal, V/U , so that the apparent particle size is

$$\varepsilon = I_s/I = V^{-1} \int_V T dV. \quad (8)$$

* In this paragraph it has been tacitly assumed that it is possible to pick out a line of scattering centres having the direction of the line joining the origin of the reciprocal lattice to the point h, k, l . For a cubic crystal this can be done accurately, and for other types of crystal to any desired degree of approximation. If equation (4) holds for directions differing slightly from that desired, but enclosing it on all sides, considerations of continuity require that it hold for the correct direction also. For a derivation in which this difficulty does not arise, see Stokes and Wilson (1944).

The physical significance of (8) is readily seen: the apparent particle size is the volume average of the thickness of the crystal measured perpendicular to the reflecting planes. This is a very elegant result, and carries conviction with it, since it seems intuitively probable that the broadening of X-ray reflections due to the smallness of the diffracting crystal will depend only on the form and orientation of the crystal, and not on its particular internal construction. The form

$$\varepsilon = V^{-1} \iint T^2 dy dz \quad . \quad . \quad . \quad (9)$$

obtained from (6) instead of (7), or that given in equation (14) below, is frequently more convenient to evaluate.

The maximum intensity as a function of θ is

$$\begin{aligned} I_0 &= (2 \cos \theta / \lambda) I_s \\ &= (2 \cos \theta / \lambda U) \int_V T dV, \quad . \quad . \quad . \quad (10) \end{aligned}$$

and the integral breadth of the reflection is

$$\begin{aligned} \beta &= 2I/I_0 \\ &= \frac{\lambda V}{\cos \theta \int_V T dV} \quad . \quad . \quad . \quad (11) \end{aligned}$$

4. The apparent particle size is easily calculated for simple geometrical shapes. For example, for a sphere it will be the same for all reflections, and given by (figure 2)

$$\begin{aligned} \varepsilon &= V^{-1} \iint T^2 dy dz = (6/\pi D^3) \int_0^{2\pi} \int_0^{D/2} (D^2 - 4r^2) r dr d\theta \\ &= \frac{12}{D^3} \left[\frac{D^4}{8} - \frac{D^4}{16} \right] \\ &= 3D/4, \quad . \quad . \quad . \quad (12) \end{aligned}$$

where D is the diameter of the sphere. It is usual, however, to take $p \equiv \sqrt[3]{V}$ as the standard 'linear dimension'

of the crystal, and in terms of this

$$\begin{aligned}\varepsilon &= \frac{3}{4} \sqrt[3]{\frac{6}{\pi}} p \\ &= 0.930p.\end{aligned}\quad (13)$$

The apparent particle size ε is thus just a little less than the actual particle size p .

For crystals other than spherical ε will depend on the indices of reflection h, k, l . For reflection from a cube

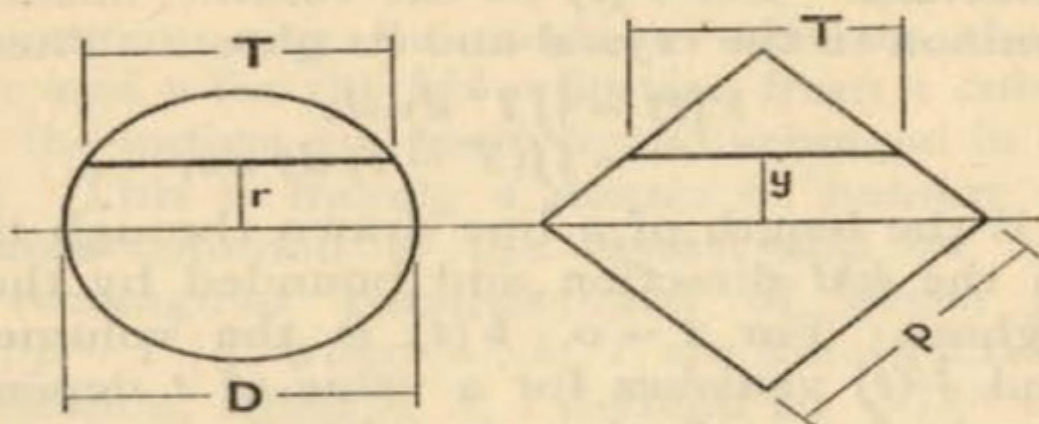


FIG. 2.—Calculation of the apparent particle size for reflections from spherical crystals and for the 110 reflections from cubic crystals.

face it is clearly p , since p is the cube edge, and for planes perpendicular to a face diagonal it is (figure 2)

$$\begin{aligned}\varepsilon &= 2p^{-3} \int_0^p \int_0^{p/\sqrt{2}} (\sqrt{2}p - 2y)^2 dy dz \\ &= 2\sqrt{2}p/3 \\ &= 0.943p.\end{aligned}\quad (14)$$

For this reflection also the apparent particle size is somewhat less than the actual.

5. For the practical calculation of the factor connecting ε and p for a general hkl reflection the form of equation (9) is not so convenient as one that can be obtained from it by a simple transformation. In figure 3, let A be the crystal, and let B be its 'ghost', shifted a distance t in

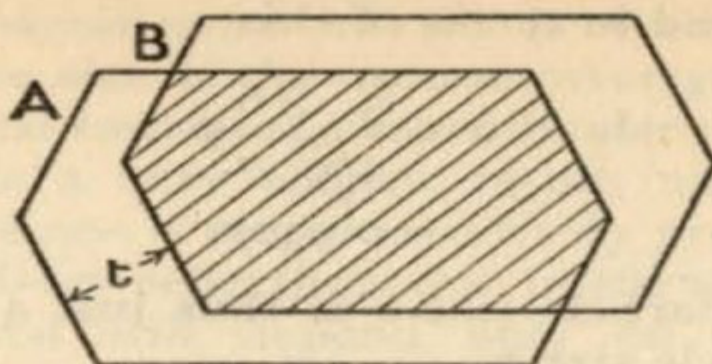


FIG. 3.—Crystal and its 'ghost'.

the hkl direction. Let $V(t)$ be the volume, shaded in the figure, common to the crystal and its ghost. Then

$$\begin{aligned} V(t) &= \iint T' dy dz \\ &= \iint (T - t) dy dz, \end{aligned} \quad (15)$$

where T' is the length of a line drawn through the point x, y, z in the hkl direction and bounded by the crystal and the ghost. For $t = 0$, $V(t)$ is the volume of the crystal, and $V(t)$ vanishes for a value of t depending on the size and shape of the crystal. Suppose now that equation (15) is integrated with respect to t from $t = 0$ to a sufficiently large value to make $V(t)$ vanish. This may be symbolized by

$$\int_0^+ V(t) dt.$$

Then
$$\int_0^+ V(t) dt = \iint \left[T \int_0^+ dt - \int_0^+ t dt \right] dy dz. \quad (16)$$

Clearly $\int_0^+ dt$ is simply T , the thickness of the crystal measured in the hkl direction through the point x, y, z , and $\int_0^+ t dt$ is $T^2/2$, so

$$\begin{aligned} \int_0^+ V(t) dt &= \frac{1}{2} \iint T^2 dy dz \\ &= V\epsilon/2. \end{aligned} \quad (17)$$

If the ghost is shifted a distance t in the opposite direction the common volume is the same as before, so the integral of $V(t)$ from a sufficiently large negative value to $t = 0$ is also $V\varepsilon/2$. Thus

$$\int_{-}^0 V(t) dt + \int_0^{+} V(t) dt,$$

or for shortness $\int V(t) dt$, is equal to $V\varepsilon$, and

$$\varepsilon = V^{-1} \int V(t) dt. \quad . \quad . \quad . \quad (18)$$

This expression may be used to evaluate the relation between ε and p for the hkl reflection from a cube. Suppose that the indices are positive and arranged in the order $h > k > l$. This is merely a matter of naming the axes. The volume common to the crystal and its 'ghost' is then a rectangular parallelepiped of edges $p - h' |t|$, $p - k' |t|$, $p - l' |t|$, where h' , k' , l' are the direction cosines of the reflection, being h , k , l divided by $\sqrt{(h^2 + k^2 + l^2)}$. The limits of integration are $t = \pm p/h'$, and the apparent particle size is therefore

$$\begin{aligned} \varepsilon &= p^{-3} \int_{-p/h'}^{+p/h'} (p - h' |t|)(p - k' |t|)(p - l' |t|) dt \\ &= \frac{2}{p^3} \left[p^4/h' - (h' + k' + l')p^4/2h'^2 + (h'k' + k'l' + l'h')p^4/3h'^3 \right. \\ &\quad \left. - h'k'l'p^4/4h'^4 \right] \\ &= \frac{\sqrt{(h^2 + k^2 + l^2)}(6h^2 - 2hk + kl - 2lh)}{6h^3} p. \quad . \quad . \quad (19) \end{aligned}$$

Table I gives values of the ratio p/ε for a number of reflections from crystals whose external form is cubic, octahedral or tetrahedral. It is somewhat modified and extended from that given by Stokes and Wilson (1942), where explicit formulae for these shapes and also for the rectangular parallelepiped are given.

TABLE I

The ratio of the true to the apparent particle size for various reflections from crystals having the form of a tetrahedron, a cube or an octahedron. For a sphere the ratio is constant at 1.0747

Reflection	Tetrahedron	Cube	Octahedron
100	1.3867	1.0000	1.1006
110	0.9806	1.0607	1.0376
111	1.2009	1.1547	1.1438
210	1.2403	1.0733	1.1075
211	1.1323	1.1527	1.1061
221	1.1556	1.1429	1.1185
310	1.3156	1.0672	1.1138
311	1.2543	1.1359	1.1211
320	1.1538	1.0698	1.0902
321	1.1119	1.1394	1.0955
410	1.3453	1.0583	1.1123
322	1.1772	1.1556	1.1304
411	1.3074	1.1174	1.1207
331	1.1135	1.1262	1.0963
421	1.2104	1.1324	1.1133
332	1.1826	1.1513	1.1334
430	1.1094	1.0667	1.0786
431	1.0878	1.1240	1.0835
510	1.3597	1.0506	1.1101

6. The line-profile, that is the intensity of reflection as a function of the angle of reflection, is given by equation 1 :

$$I(\theta) = (2 \cos \theta / \lambda) I(S),$$

where $I(S)$ is the integral of the intensity of reflection in reciprocal space over the region bounded by spheres of radii S and $S + dS$. Equation 5 gives a general expression for $I(S)$,

$$\frac{1}{U} \iint \frac{\sin^2 (\pi Ts)}{(\pi s)^2} dy dz,$$

but, like the corresponding equation (9) for the apparent particle size, this expression is not usually the most convenient to evaluate. One alternative form, corresponding to equation (7), is

$$I(S) = \frac{1}{U} \int_V T \frac{\sin^2 (\pi Ts)}{(\pi Ts)^2} dV, \quad (20)$$

where the integration extends throughout the volume of the crystal, but the most useful form is probably

$$I(S) = U^{-1} \int V(t) \cos(2\pi st) dt, \quad (21)$$

where $V(t)$ is the volume common to the crystal and its 'ghost' shifted a distance t in the hkl direction, and the limits of integration are the positive and negative values of t for which $V(t)$ vanishes. This may be shown by the same method as was used in the preceding paragraph. Since

$$V(t) = \iint (T - t) dy dz$$

(equation 15),

$$\begin{aligned} \int_0^+ V(t) \cos(2\pi st) dt &= \iint \left[\int_0^+ (T - t) \cos(2\pi st) dt \right] dy dz \\ &= \iint \left[T \int_0^+ \cos(2\pi st) dt - \int_0^+ t \cos(2\pi st) dt \right] dy dz \\ &= \iint \left[T \frac{\sin(2\pi sT)}{2\pi s} - T \frac{\sin(2\pi sT)}{2\pi s} + \int_0^+ \frac{\sin(2\pi st)}{2\pi s} dt \right] dy dz \\ &= \frac{1}{4} \iint \frac{1 - \cos(2\pi sT)}{(\pi s)^2} dy dz \\ &= \frac{1}{2} \iint \frac{\sin^2(\pi sT)}{(\pi s)^2} dy dz. \quad (22) \end{aligned}$$

Since $\int_{-}^0 V(t) \cos(2\pi st) dt$ is equal to $\int_0^+ V(t) \cos(2\pi st) dt$,

$$\begin{aligned} \int V(t) \cos(2\pi st) dt &= \iint \frac{\sin^2(\pi sT)}{(\pi s)^2} dy dz \\ &= UI(S), \quad (23) \end{aligned}$$

as it was required to show.

7. Little attention has so far been given to line-profiles, since integral breadths are easier to investigate experimentally. Equation (21) may, however, be evaluated for any given value of $V(t)$. Let τ be the value of t for which

$V(t)$ vanishes. Then, by repeated integration by parts,

$$\begin{aligned}
 I(S) &= U^{-1} \int V(t) \cos(2\pi st) dt \\
 &= 2U^{-1} \int_0^\tau V(t) \cos(2\pi st) dt \\
 &= 2U^{-1} \left[V(t) \frac{\sin(2\pi st)}{2\pi s} + V'(t) \frac{\cos(2\pi st)}{(2\pi s)^2} \right. \\
 &\quad \left. - V''(t) \frac{\sin(2\pi st)}{(2\pi s)^3} - V'''(t) \frac{\cos(2\pi st)}{(2\pi s)^4} \right. \\
 &\quad \left. + \int V^{iv}(t) \frac{\cos(2\pi st)}{(2\pi s)^4} dt \right]_0^\tau, \quad (24)
 \end{aligned}$$

where the primes denote differentiation with respect to t . The first term in the square brackets vanishes at both limits, since $V(\tau)$ is zero. For ordinary crystal shapes, such as all those mentioned in paragraph 5, $V(t)$ is a cubic in t , so that V''' is a constant, $V^{iv}(t)$ is identically zero and the final integral vanishes. The line-profile is therefore given by

$$\begin{aligned}
 I(S) &= \frac{1}{2} U^{-1} \left[-(\pi s)^{-2} V'(0) + (\pi s)^{-2} \cos(2\pi s\tau) V'(\tau) \right. \\
 &\quad \left. - \frac{1}{2} (\pi s)^{-3} \sin(2\pi s\tau) V''(\tau) + \frac{1}{4} (\pi s)^{-4} \{1 - \cos(2\pi s\tau)\} V''' \right]. \quad (25)
 \end{aligned}$$

It is easy to find $I(S)$ for any particular case by substituting the appropriate values for $V(t)$ and τ in equation (25). For example, if the crystal is a cube of edge p ,

$$V(t) = (p - h't)(p - k't)(p - l't)$$

and $\tau = p/h'$ (paragraph 5), so

$$\begin{aligned}
 V'(t) &= -h'(p - k't)(p - l't) - k'(p - l't)(p - h't) \\
 &\quad - l'(p - h't)(p - k't),
 \end{aligned}$$

$$V'(0) = -p^2(h' + k' + l'),$$

$$V'(\tau) = -p^2(h' - k')(h' - l')/h',$$

$$V''(t) = 2h'k'(p - l't) + 2k'l'(p - h't) + 2l'h'(p - k't),$$

$$V''(\tau) = 2p(h'k' - 2k'l' + l'h'),$$

$$V''' = -6h'k'l'.$$

The line-profile is therefore

$$\begin{aligned}
 I(S) &= \frac{1}{2U} \left[\frac{p^2}{(\pi s)^2} \left\{ h' + k' + l' - \frac{(h' - k')(h' - l')}{h'} \cos(2\pi p s / h') \right\} \right. \\
 &\quad \left. - \frac{p}{(\pi s)^3} (h'k' - 2k'l' + l'h') \sin(2\pi p s / h') \right. \\
 &\quad \left. - \frac{3h'k'l'}{2(\pi s)^4} \left\{ 1 - \cos(2\pi p s / h') \right\} \right] \\
 &= \frac{p^4 \sqrt{h^2 + k^2 + l^2}}{2Uh} \left[\frac{1}{\psi^2} \left\{ \frac{h+k+l}{h} - \frac{(h-k)(h-l)}{h^2} \cos 2\psi \right\} \right. \\
 &\quad \left. - \frac{1}{\psi^3} \frac{hk - 2kl + lh}{h^2} \sin 2\psi - \frac{3}{2\psi^4} \frac{kl}{h^2} (1 - \cos 2\psi) \right] \quad (26)
 \end{aligned}$$

where $\psi = (\pi p s \sqrt{h^2 + k^2 + l^2})/h$. It will be remembered that h, k, l are here the positive values of the indices arranged in the order $h > k > l$.

The asymptotic value of $I(S)$, that is the value about which it oscillates for large values of s , is given by the first term only of equation (25),

$$I(S) \sim - \frac{V'(0)}{2(\pi s)^2 U}, \quad . \quad . \quad . \quad (27)$$

so $I(S)$ falls off as s^{-2} . The coefficient of s^{-2} is positive, since $V(t)$ has its greatest value for $t = 0$, and $V'(t)$ must be negative for $t = 0$. In fact, it is easily seen that $-V'(0)$ is the area of the projection of the crystal on the reflecting plane. Equation (27) may therefore be written

$$I(S) \sim A/2U(\pi s)^2, \quad . \quad . \quad . \quad (28)$$

where A is this area. An alternative expression for the asymptotic behaviour of $I(S)$ may be got from equation (20). For s large $\sin(\pi Ts)$ undergoes rapid alterations in value with changes in T (that is, with change in position in the crystal), and in the integration over the volume of the crystal $\sin^2(\pi Ts)$ may be replaced by its average value,

which is one-half. Equation (20) becomes

$$I(S) \sim \frac{1}{2U(\pi s)^2} \int_V \frac{dV}{T}, \quad (29)$$

which is an interesting contrast to equation (7). The value of $I(S)$ for s small depends on the volume average of the thickness of the crystal measured perpendicular to the reflecting planes; its value for s large depends on the volume average of the reciprocal of the same quantity.

It is not to be expected that the small oscillations about the mean value caused by the trigonometric terms in the expressions for the line-profile would ever be observed. Even if all the crystals forming the powder specimen had the same shape it is unlikely that they would all have the same size, and variations in the size would cause the oscillations to come at different places and so smooth out the line-profile.

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CHAPTER V

MISTAKES IN LAYER STRUCTURES : GENERAL CALCULATION

MISTAKES IN THREE DIMENSIONS : POWDER PHOTOGRAPHS

1. So far it has been possible to treat each unit cell of a crystal as a single scattering centre, and all unit cells as identical. If, however, the unit cells are not identical, it is necessary to consider the actual distribution of atoms in the cell and the combination of scattered rays of different amplitudes. The effect of the distribution of atoms can be summed up in a quantity called the 'structure amplitude'. The amplitude of the X-rays scattered by each atom can be calculated as a function of the scattering angle if the distribution of electrons in the atom is known. It is more or less proportional to the atomic number, and is greatest at low angles (James, pp. 65-72). It is generally denoted by f , with a subscript to distinguish different atoms. Tables giving f as a function of $\sin \theta / \lambda$ have been prepared for most atoms (*Internationale Tabellen*, vol. II, pp. 571-4; Bragg, 1933, pp. 329-34). If f is known for each atom, the effect of their different positions within the unit cell can be determined. Suppose that there are atoms of scattering factors f_1, f_2, \dots, f_n at positions in the unit cell $x_1, y_1, z_1; x_2, y_2, z_2; \dots; x_n, y_n, z_n$; where x, y, z are given as fractions of the edges of the unit cell. For the hkl reflection the rays scattered at $(1, 1, 1)$ would be advanced in phase by $2\pi(h + k + l)$ radians with respect to those scattered at $(0, 0, 0)$, so the rays scattered at (x, y, z) are advanced in phase by $2\pi(hx + ky + lz)$ radians. The resultant of the rays scattered by the various atoms can be constructed graphically as shown in figure 1. Each atom is represented by a line of length f at an angle of $2\pi(hx + ky + lz)$

to the horizontal, and the resultant F is represented in magnitude by the length of the line joining the beginning of f_1 to the end of f_n , and in phase δ by the angle that

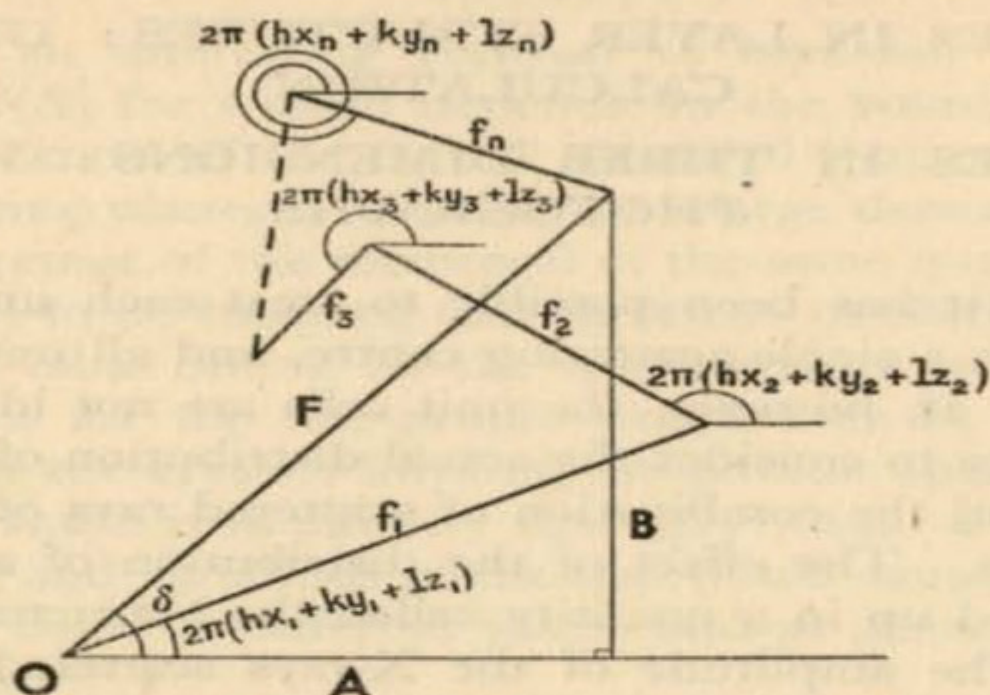


FIG. 1.—Graphical construction for the structure amplitude.

this line makes with the horizontal. Trigonometrically expressed,

$$F^2 = A^2 + B^2, \quad (1)$$

$$\cos \delta = A/|F|, \quad \sin \delta = B/|F|, \quad (2)$$

where

$$A = f_1 \cos 2\pi(hx_1 + ky_1 + lz_1) + f_2 \cos 2\pi(hx_2 + ky_2 + lz_2) + \cdots + f_n \cos 2\pi(hx_n + ky_n + lz_n), \quad (3)$$

$$B = f_1 \sin 2\pi(hx_1 + ky_1 + lz_1) + f_2 \sin 2\pi(hx_2 + ky_2 + lz_2) + \cdots + f_n \sin 2\pi(hx_n + ky_n + lz_n) \quad (4)$$

These expressions may be simplified if the positions of some or all of the atoms are related by the symmetry elements of the space group. For example, in many cases the origin of the unit cell is a centre of symmetry, and an atom at the point (x, y, z) implies another at the point $(1 - x, 1 - y, 1 - z)$. In the equation for B , therefore, for every term $f \sin 2\pi(hx + ky + lz)$ there is another

$$f \sin 2\pi\{h(1 - x) + k(1 - y) + l(1 - z)\} = -f \sin 2\pi(hx + ky + lz),$$

which cancels it, so that B is zero and δ is a multiple of π . In such cases it is not really necessary to consider the phase angle. Since the lines representing the structure amplitudes are all horizontal, differing merely in direction, they may be added algebraically instead of trigonometrically. They are taken as positive if $\delta = 0$, negative if $\delta = \pi$. In these cases then $F = A$, $B = 0$. Even if B does not vanish for all reflections it is always possible to choose a new origin in the unit cell so that it vanishes for the reflection in which one is immediately interested. A shift of origin to the point (ξ, η, ζ) would decrease all the angles in figure 1 by $2\pi(h\xi + k\eta + l\zeta)$; that is, it would merely rotate the figure through this angle. Such a rotation would not change the magnitude of F , but the angle δ could be reduced to zero by a proper choice of the new origin.

The simplifications produced by all the possible combinations of symmetry elements have been tabulated (*Internationale Tabellen*, vol. I; Lonsdale, 1936). It may happen that for some values of h, k, l both A and B are zero, and hence that there is no diffracted beam even though the conditions for reflection derived in chapter II are satisfied. The corresponding point of the reciprocal lattice is then unaccompanied by any region of X-ray diffraction. Such reflections of zero intensity are called *absences*. They are of great help in fixing the symmetry of the crystal, but care has to be taken not to confuse absences due to the symmetry of the crystal with 'accidental' absences, which occur when F^2 for a particular reflection happens to be too small to be observed. We are, however, concerned not with the determination of structures, but with the reciprocal space corresponding to a crystal in which F has different values in different unit cells.

2. Mistakes are particularly frequent among the 'layer structures'. In these the crystal can be regarded as consisting of a number of layers, the forces holding each layer together being usually much greater than those holding the separate layers together. Examples are some silicates such

as the micas, cadmium iodide, graphite, and hexagonal cobalt. If the forces between the layers are weak the layers may be displaced parallel to themselves, the arrangement of atoms within the layer being maintained, but the proper sequence of atoms in passing from one layer to the next being impaired. Even if the forces between the layers are strong, there may be several positions in which one layer can fit on to that below it without much difference in energy, and so occasional mistakes are possible. Cobalt is an example of this. It consists of close-packed planes of atoms, such as those shown in figure 2. If a plane of atoms

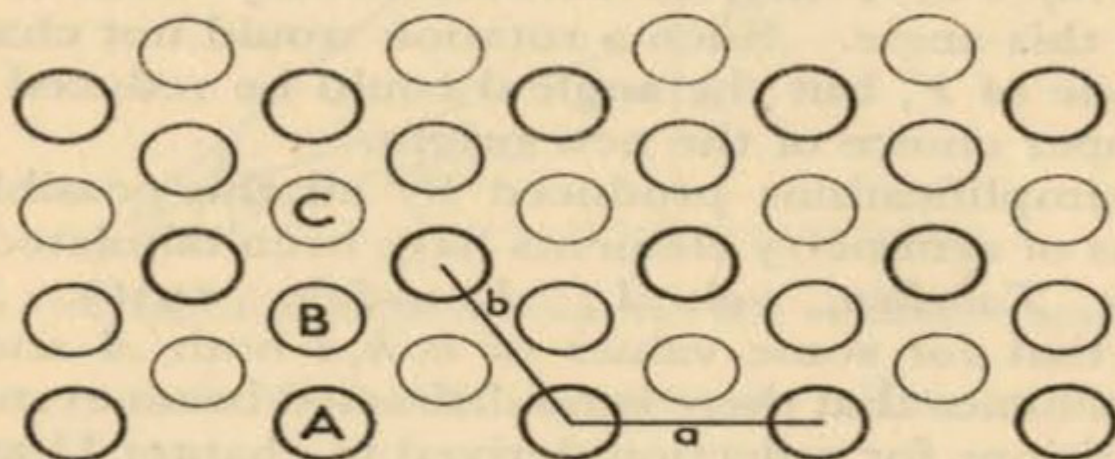


FIG. 2.—Possible positions of planes of atoms in close packing.

has the position *A*, the succeeding one can take either the position *B* or the position *C*. Suppose it takes the position *B*. The third plane could take either the position *C* or *A*. If the cobalt is in the hexagonal modification it should take the position *A*, and successive planes should maintain the sequence *ABABABABA...*. As far as the atoms in contact are concerned, however, the combination *AB* can be followed equally well by *A* or *C*, and it would not be surprising if an occasional plane forgot to consult the atoms with which it was not in contact, and settled down in the wrong place. Photographs of hexagonal cobalt do show peculiarities most easily explicable by mistakes of this kind. The layer silicates have much more complicated structures, but many of them also have three (or perhaps

six) possible positions of equilibrium. With some of them there is another possibility of mistakes. Layers of water or other substances can be adsorbed in the spaces between the layers, thus increasing the interlayer spacing. If the number of layers of water molecules is the same in every interlayer space the crystal remains perfect, but if the number of layers of water molecules varies there will be erratic variations in the interlayer spacing.

3. Let us first consider a hypothetical case in which the a and b axes lie in the plane of the layer and c is perpendicular to it, and the mistake consists of a shift of the layer by half the b axis. If F is the structure factor of a cell in an unshifted layer, the structure factor of a cell in a shifted layer is easily seen to be $(-)^k F$, since the y -coordinate of every atom is increased by $1/2$, and both A and B are changed in sign for k odd, and are unchanged for k even. If we try to calculate the amplitude of reflection by the method of chapter III, paragraph 4, we find that the summations for lines parallel to the a and b axes in the n^{th} layer go through successfully, leading to the expression

$$F_n \cdot \frac{\sin(\pi Xu/a)}{\pi u} \cdot \frac{\sin(\pi Yv/b)}{\pi v},$$

where F_n is F or $(-)^k F$ depending on whether or not the n^{th} layer is a shifted layer, but the third step, of adding the amplitudes diffracted by successive layers to give the dependence on w , cannot be taken, since the layers are not identical. As we are considering the effect of mistakes on reciprocal space, not the effect of small particle size, we may suppose that X , Y and Z are large, and the result therefore means that the reflection is practically concentrated into a region with very little extension in the directions of a^* and b^* , but that there may be a considerable spread in the direction of c^* . We have now to find some way of estimating this.

Suppose that the crystal starts with a layer in the 'right' position, and that each added layer tends to be in the right

position, but that there is a chance α of its going into the 'wrong' position. If it goes into the wrong position, every layer after it will go into the wrong position, until there is another mistake, which restores the layers to the right position. Suppose that R_n is the probability of the n^{th} added layer being in the right place, and W_n the probability of its being in the wrong place. Clearly

$$R_n + W_n = 1 \quad . \quad . \quad . \quad (5)$$

The probability of the $(n+1)^{\text{th}}$ added layer being right can be calculated as follows. If the n^{th} added layer is right the $(n+1)^{\text{th}}$ will be right unless there is a mistake, and if the n^{th} added layer is wrong the $(n+1)^{\text{th}}$ will be right only if there is a mistake. The probability of the $(n+1)^{\text{th}}$ being right is therefore the probability of the n^{th} being right multiplied by the probability of no mistake, plus the probability of the n^{th} being wrong multiplied by the probability of there being a mistake. In symbols this becomes

$$\begin{aligned} R_{n+1} &= (1 - \alpha)R_n + \alpha W_n \\ &= (1 - \alpha)R_n + \alpha(1 - R_n) \\ &= \alpha + (1 - 2\alpha)R_n \quad . \quad . \quad . \quad (6) \end{aligned}$$

This equation may be solved by trying a solution of the form

$$R_n = P + Q\rho^n \quad . \quad . \quad . \quad (7)$$

where P , Q and ρ are constants to be determined. Substitution gives $P = \frac{1}{2}$, $\rho = 1 - 2\alpha$, so

$$R_n = \frac{1}{2} + Q(1 - 2\alpha)^n \quad . \quad . \quad (8)$$

Since R_0 is 1, the starting layer being correct, Q must have the value $\frac{1}{2}$, and

$$R_n = \frac{1}{2} \{1 + (1 - 2\alpha)^n\} \quad . \quad . \quad (9)$$

In the next paragraph the average value of the product of the F 's of two layers separated by n interlayer spaces will be needed. This is clearly F^2 multiplied by the probability of the two layers being the same (that is, both right

or both wrong), plus $(-)^k F^2$ multiplied by the probability of the two layers being different. A little consideration shows that these probabilities are R_n and W_n , so that the required average is

$$F^2 R_n + (-)^k F^2 (I - R_n) = F^2, \quad k \text{ even}, \quad (10)$$

$$= (1 - 2\alpha)^n F^2, \quad k \text{ odd.} \quad (11)$$

4. Let us now try to find the intensity of reflection for $w = 0$, that is at the point where the intensity is concentrated for a perfect crystal. The amplitude is given by

$$G = F_1 + F_2 + F_3 + \dots + F_N, \quad . \quad . \quad (12)$$

where $N = Z/c$ and F_n , the structure factor of the n^{th} layer, is equal to F for k even, and is either F or $-F$ for k odd. If k is even therefore $G = NF = ZF/c$, just as for a perfect crystal. If k is odd the terms in equation (12) will be positive for a while, then negative for a while, positive again, and so on, so that the sum is indeterminate. It is, however, possible to find its probable value, or rather its probable value without regard to sign. Depending on how the mistakes occur, G could have any value between $-NF$ and $+NF$, and its average value will be zero, but usually it will have some finite sum either positive or negative. In calculating the X-ray intensity the sign does not matter, and it is the average value of G^2 that is wanted. Squaring equation (12) gives

$$G^2 = F_1^2 + F_2^2 + F_3^2 + \cdots + F_N^2 + 2(F_1F_2 + F_2F_3 + F_3F_4 + \cdots + F_{N-1}F_N) + 2(F_1F_3 + F_2F_4 + F_3F_5 + \cdots + F_{N-2}F_N) + \cdots + 2F_1F_N, \quad (13)$$

where the terms have been arranged so that in the first line the two F 's multiplied together refer to the same layer, in the second they belong to adjacent layers, in the third there is one intervening layer, and so on. Suppose that J_m is the average value of the product of the F 's of two

layers separated by m interlayer spaces. . Then

$$G^2 = NJ_0 + 2(N-1)J_1 + 2(N-2)J_2 + \cdots + 2J_{N-1}. \quad (14)$$

For the particular mistake considered in the last paragraph J_m was found to be

$$J_m = (1 - 2\alpha)^m F^2, \quad . \quad . \quad . \quad (11)$$

so

$$G^2 = F^2[2\{N + (N-1)(1-2\alpha) + (N-2)(1-2\alpha)^2 + \cdots + (1-2\alpha)^{N-1}\} - N]. \quad (15)$$

The expression within the curly brackets is a combined arithmetic-geometric series, and it is not difficult to find its sum. In the present case, however, N is large and $(1-2\alpha)^m$ decreases rapidly, so it may for practical purposes be regarded as geometric series of the form $N(1-2\alpha)^m$ summed to infinity, and

$$\begin{aligned} G^2 &= 2NF^2\{1 + (1-2\alpha) + (1-2\alpha)^2 + \cdots\} \\ &= 2NF^2/2\alpha \\ &= F^2Z/c\alpha. \quad . \quad . \quad . \quad . \quad . \quad (16) \end{aligned}$$

The total intensity of the reflection is F^2Z/c , so its integral breadth in w is α . Thus the greater the chance of a mistake the more the region of appreciable intensity of reflection is spread out along the c^* axis in reciprocal space.

5. Having found the maximum intensity of reflection as a function of position in reciprocal space, that is $G^2(w) \equiv I(w)$ for $w = 0$, let us try to evaluate $I(w)$ for an arbitrary value of w . In this case each layer will be reflecting $2\pi w$ out of phase with the preceding one, and the intensity of reflection as a function of w will be given by

$$I(w) = G^2(w) = A^2 + B^2,$$

where

$$\begin{aligned} A &= F_1 + F_2 \cos 2\pi w + F_3 \cos 4\pi w + F_4 \cos 6\pi w + \cdots, \\ B &= F_2 \sin 2\pi w + F_3 \sin 4\pi w + F_4 \sin 6\pi w + \cdots. \end{aligned}$$

By squaring and arranging terms as in equation (13) above

this becomes

[illegible]

so

$$\frac{a^2 + b^2}{a^2} \int_0^\infty e^{-ax} \cos bx \, dx = \frac{1}{a},$$

$$\int_0^\infty e^{-ax} \cos bx \, dx = a/(a^2 + b^2). \quad (22)$$

In the present case $a = \gamma$, $b = 2\pi w$, so

$$I(w) = \frac{2NF^2\gamma}{\gamma^2 + (2\pi w)^2} \quad (23)$$

$$= \frac{\alpha ZF^2}{c(\alpha^2 + \pi^2 w^2)} \quad (24)$$

For $w = 0$ this reduces to equation (16), as it should. The course of $I(w)$ as a function of w is shown in figure 3. It is very similar to that of $\sin^2 \pi Nu/(\pi u)^2$, shown in figure 2 of chapter III, except that it does not oscillate. Both go to

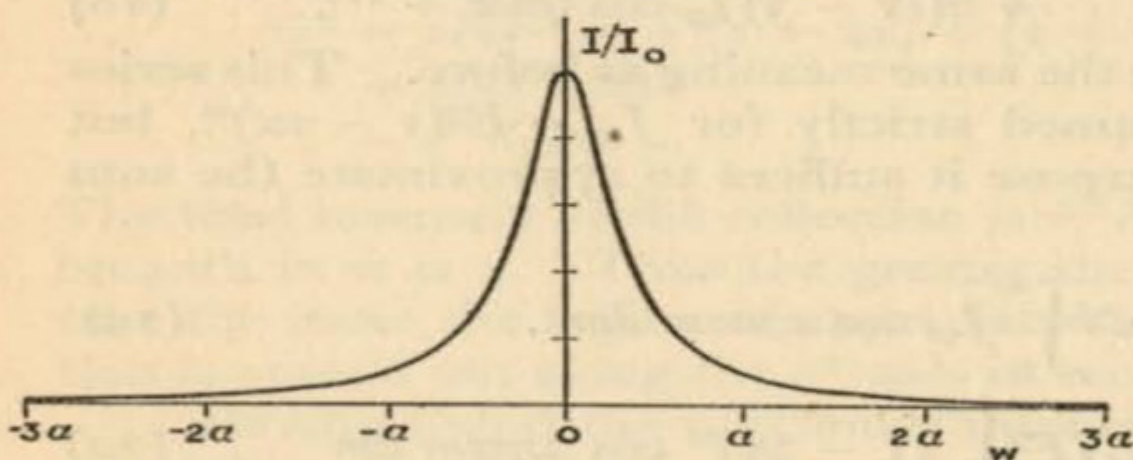


FIG. 3.—Variation of intensity as a function of w for a layer structure with mistakes.

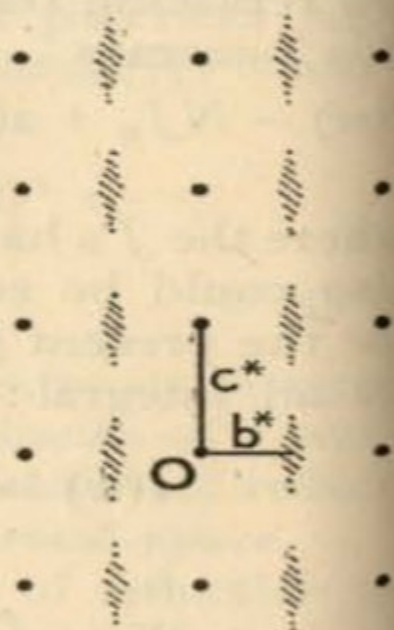


FIG. 4.—Portion of the reciprocal lattice for a layer structure with mistakes.

zero as the inverse square of the variable for large values of the variable. The broadening of the reflections differs from that due to a small thickness of the crystal in the c direction in that only those reflections with k odd are affected. A section of the reciprocal lattice is shown in figure 4.

It is perhaps worth while to check that the total intensity of the reflection is actually ZF^2/c , as this gives some assurance that the approximations used have not introduced serious errors. The total intensity is

$$I = \int_{-}^{+} I(w) dw = (\alpha ZF^2/c) \int_{-}^{+} (\alpha^2 + \pi^2 w^2)^{-1} dw$$

$$= (\alpha ZF^2/c)(\pi\alpha)^{-1} \left[\text{arc tan } (\pi w/\alpha) \right]_{-}^{+}.$$

At the upper limit $\pi w/\alpha$ has a large positive value, so that $\text{arc tan } (\pi w/\alpha)$ is practically $\pi/2$, and at the lower limit it has a large negative value, so that $\text{arc tan } (\pi w/\alpha)$ is practically $-\pi/2$. The total value of the integral is therefore ZF^2/c .

6. In the foregoing paragraphs the calculation of the intensity of reflection from a layer structure containing mistakes has been carried through in detail for a particularly simple variety of mistake. The method adopted is, however, of general application in the calculation of the intensity of reflection from a layer structure containing mistakes. If $A_1, A_2, \dots, B_1, B_2, \dots$, are the A and B parts of the structure factors of the unit cells in the various planes (equations (1)–(4) above), and c^* is taken perpendicular to the layers, the contribution of the n^{th} layer to the A part of the total amplitude of reflection is (figure 5)

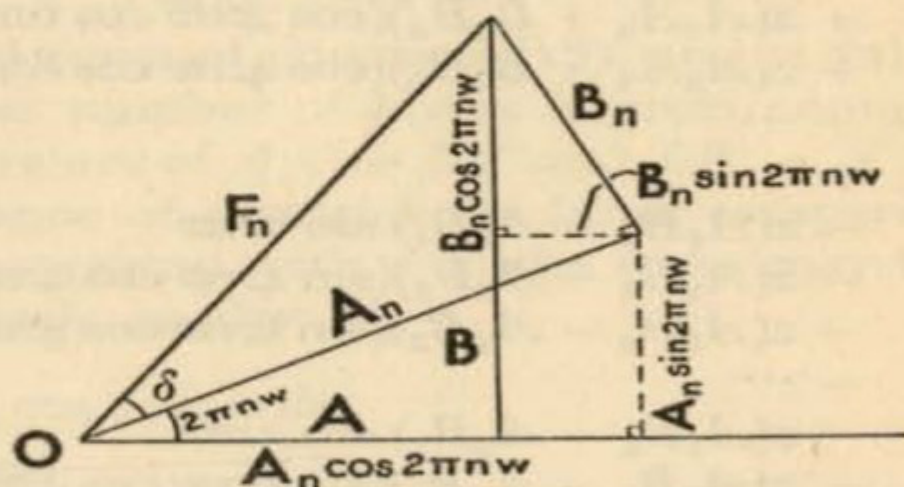


FIG. 5.—Construction for the A and B parts of the amplitude reflected by the n^{th} layer. In this figure $2\pi nw$ should be $2\pi(n-1)w$.

$$A_n \cos 2\pi(n-1)w - B_n \sin 2\pi(n-1)w,$$

and the B part is

$$A_n \sin 2\pi(n-1)w + B_n \cos 2\pi(n-1)w,$$

and the intensity of reflection as a function of w is, the terms being arranged as before,

$$\begin{aligned} I(w) &= G^2(w) = A^2(w) + B^2(w) \\ &= (A_1 + A_2 \cos 2\pi w + A_3 \cos 4\pi w + A_4 \cos 6\pi w + \dots \\ &\quad - B_2 \sin 2\pi w - B_3 \sin 4\pi w - B_4 \sin 6\pi w - \dots)^2 \\ &\quad + (A_2 \sin 2\pi w + A_3 \sin 4\pi w + A_4 \sin 6\pi w + \dots \\ &\quad + B_1 + B_2 \cos 2\pi w + B_3 \cos 4\pi w + B_4 \cos 6\pi w + \dots)^2 \\ &= (A_1^2 + B_1^2) + (A_2^2 + B_2^2) + (A_3^2 + B_3^2) + \dots \\ &\quad + 2(A_1 A_2 + B_1 B_2) \cos 2\pi w \\ &\quad + 2(A_2 A_3 + B_2 B_3)(\cos 2\pi w \cos 4\pi w + \sin 2\pi w \sin 4\pi w) \\ &\quad + 2(A_3 A_4 + B_3 B_4)(\cos 4\pi w \cos 6\pi w + \sin 4\pi w \sin 6\pi w) \\ &\quad + \dots \\ &\quad + 2(A_1 A_3 + B_1 B_3) \cos 4\pi w \\ &\quad + 2(A_2 A_4 + B_2 B_4)(\cos 2\pi w \cos 6\pi w + \sin 2\pi w \sin 6\pi w) \\ &\quad + 2(A_3 A_5 + B_3 B_5)(\cos 4\pi w \cos 8\pi w + \sin 4\pi w \sin 8\pi w) \\ &\quad + \dots \\ &\quad + \dots \\ &\quad - 2(A_1 B_2 - A_2 B_1) \sin 2\pi w \\ &\quad - 2(A_2 B_3 - A_3 B_2)(\sin 4\pi w \cos 2\pi w - \cos 4\pi w \sin 2\pi w) \\ &\quad - 2(A_3 B_4 - A_4 B_3)(\sin 6\pi w \cos 4\pi w - \cos 6\pi w \sin 4\pi w) \\ &\quad - \dots \\ &\quad - 2(A_1 B_3 - A_3 B_1) \sin 4\pi w \\ &\quad - 2(A_2 B_4 - A_4 B_2)(\sin 6\pi w \cos 2\pi w - \cos 6\pi w \sin 2\pi w) \\ &\quad - 2(A_3 B_5 - A_5 B_3)(\sin 8\pi w \cos 4\pi w - \cos 8\pi w \sin 4\pi w) \\ &\quad - \dots \\ &\quad - \dots \\ &= (A_1^2 + B_1^2) + (A_2^2 + B_2^2) + (A_3^2 + B_3^2) + \dots \\ &\quad + 2 \cos 2\pi w [(A_1 A_2 + B_1 B_2) + (A_2 A_3 + B_2 B_3) \\ &\quad \quad + (A_3 A_4 + B_3 B_4) + \dots] \\ &\quad + 2 \cos 4\pi w [(A_1 A_3 + B_1 B_3) + (A_2 A_4 + B_2 B_4) \\ &\quad \quad + (A_3 A_5 + B_3 B_5) + \dots] \\ &\quad + 2 \cos 6\pi w [(A_1 A_4 + B_1 B_4) + (A_2 A_5 + B_2 B_5) \\ &\quad \quad + (A_3 A_6 + B_3 B_6) + \dots] \\ &\quad + \dots \end{aligned}$$

in a way appropriate to the particular problem. From the definitions of J_m and K_m it is obvious that $J_{-m} = J_m$, and $K_{-m} = -K_m$, so that equation (28) may be written more symmetrically as

$$I(w) = N \int_{-\infty}^{+\infty} (J_m \cos 2\pi w m - K_m \sin 2\pi w m) dm$$

or

$$I(w) = N \int (J_m \cos 2\pi w m - K_m \sin 2\pi w m) dm \quad . \quad (29)$$

for short. In very many cases, as in the example used in paragraphs 4 and 5, K_m is zero and the terms involving it vanish. In most of the problems to be considered in the following chapter J_m has the form $J_0 e^{-\gamma m}$, as in equation (21) above, and equation (28) becomes

$$I(w) = \frac{2N\gamma J_0}{\gamma^2 + (2\pi w)^2} \quad . \quad . \quad . \quad (30)$$

The maximum value of this is $2NJ_0/\gamma$, and the total intensity is NJ_0 , so that the integral breadth in w is $\gamma/2$.

7. The general effect of mistakes in layer structures will now be obvious. Reflections whose structure amplitude is not affected by the mistake in question (for example, all reflections with k even in the example considered above) will be unaffected, and the spots or lines on the X-ray photograph will be as sharp as if the crystal were perfect. On the other hand, reflections whose structure amplitude is affected by the mistake will be drawn out in reciprocal space in a direction perpendicular to the layers. The amount of the spread will depend on the frequency of the mistakes and the amount of the change in the structure amplitude; in the simple example considered in paragraphs 4 and 5 all reflections with k odd were drawn out into streaks in reciprocal space of length of the order of c^*/α . The corresponding spots on the X-ray photograph will in general be drawn out also, or the lines in the powder photograph broadened, but the magnitude of the effect depends on the angle that the streak makes with the surface of the sphere of reflection, and is most readily

discussed in connection with particular examples, as is done in the following chapter. If K_m is not zero the reflection is displaced as well as broadened. This is readily seen from any of equations (26) to (29), since $I(-w)$ is not equal to $I(w)$ unless the terms involving sines vanish. One or two examples of displacement are discussed in chapter VII.

8. Besides layer structures with mistakes, which may be described as mistakes in one dimension, examples are known of substances exhibiting mistakes in three dimensions. One of these is an alloy of gold and copper, in the proportion of one gold atom to three copper atoms. The nature of the mistakes may be

understood from figure 6, which represents one unit cell of the crystal. The cell is cubic and contains four atoms, distinguished by the letters A , B , C , D . (At first sight there appear to be twelve atoms, but

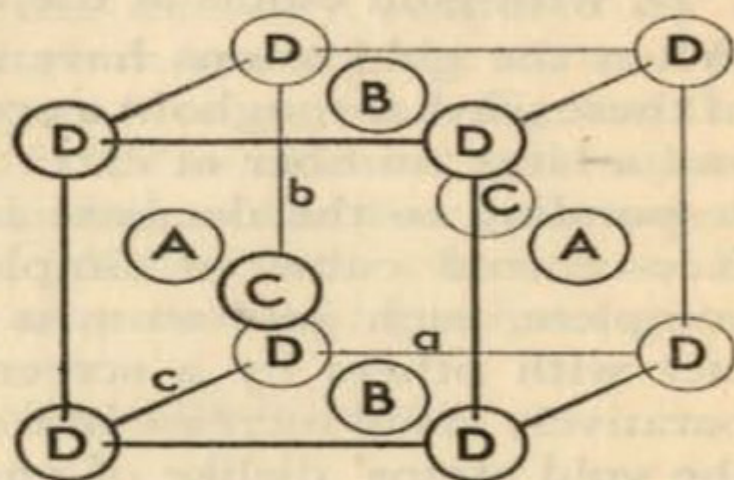


FIG. 6.—Unit cell of AuCu_3 .

only one-eighth of each atom marked D is really inside the cell, the remaining seven-eighths being in neighbouring cells. Similarly, only one-half of each atom marked A , B , or C is inside the cell.) On the average, one of these four atoms will be gold and three will be copper. At high temperatures the gold and copper atoms are mixed at random, and powder photographs show only the reflections corresponding to a face-centred cubic structure. At lower temperatures the gold atoms, behaving as if they were larger than the copper atoms, avoid one another, and in an ideal crystal would all settle into position A , or all into position B , or all into position C , or all into position D , the three positions not occupied by gold atoms being occupied by copper atoms. Thus at high temperatures any position, say A , is occupied on the average by one-

quarter of a gold atom and three-quarters of a copper atom, and at low temperatures either always by gold or always by copper. There are therefore at low temperatures four distinct types of unit cell :

- A*, with gold atoms in the centre of the face perpendicular to the *a* axis,
- B*, with gold atoms in the centre of the face perpendicular to the *b* axis,
- C*, with gold atoms in the centre of the face perpendicular to the *c* axis, and
- D*, with gold atoms at the cube corners.

When the gold atoms have sorted themselves out in one of these ways throughout a crystal it is said to be 'ordered', and a large number of extra X-ray reflections appear, corresponding to the decrease in symmetry from statistically face-centred cubic to simple cubic. If the ordering is complete, each gold atom is entirely separated from contact with others by a screen of copper atoms. A comparatively small increase in temperature is able to overcome the gold atoms' dislike of one another's company, so that it would not be surprising if within an ordered single crystal mistakes occurred such that the type of order varied from place to place. This is found to be the case, and by proper heat treatment it is easy to put the alloy into a state in which the reflections common to the ordered and disordered state are sharp, but those characteristics of the ordered state only are more or less diffuse. One or two other substances exhibiting mistakes of this type are known, but they are much rarer than layer structures with mistakes, perhaps because it is only possible to build up three-dimensional mistakes with exactly four types of unit cell (Bragg, 1940).

9. The intensity of reflection from such a structure as a function of position in reciprocal space could be treated by methods similar to those of paragraph 6 above, but the double series there, already sufficiently clumsy, are replaced by sixfold series, and become almost unmanageable. Consideration of this problem will therefore be postponed to

chapter VII, where more advanced mathematical methods are introduced. Line broadening in powder photographs may, however, be treated here by essentially the same argument as was applied previously in connection with particle size broadening (chapter IV). To calculate the integral breadth of the hkl reflection, we calculate the intensity scattered with S between S and $S + dS$ by a single line of unit cells parallel to the radius vector joining the point h, k, l of the reciprocal lattice to the origin, and sum for all parallel lines. If paragraph 6 is re-read, it will be seen that the calculation of the intensity scattered by a single line of cells goes through in exactly the same way as the calculation of $I(w)$, except that J_m and K_m are the mean values of $AA' + BB'$ and $AB' - A'B$ for cells separated by m repeat distances parallel to the line, instead of perpendicular to the layers. With axes chosen as in paragraph 3, chapter IV, one may rewrite equation (27) as

$$H(u) du = (2/a) \int_0^T (T-t) J(t) \cos (2\pi tu/a) dt du \\ - (2/a) \int_0^T (T-t) K(t) \sin (2\pi tu/a) dt du \quad . \quad (31)$$

where a is the repeat distance in the direction of the line, $T = Na$ is the length of the line, $t = ma$, and u is written in place of w to conform to the notation of the previous chapter. The interpretation of $J(t)$ and $K(t)$ is fairly obvious; they are the mean values of $AA' + BB'$ and $AB' - A'B$ for cells separated by a distance t along the line. Equation (31) is analogous to equation (3) of chapter IV, and $I(S)$ is obtained from it in the same way:

$$I(S) = (a/U) \iint H(u) dy dz \\ = (2/U) \iiint_0^T (T-t) J(t) \cos (2\pi tu/a) dt dy dz \\ - (2/U) \iiint_0^T (T-t) K(t) \sin (2\pi tu/a) dt dy dz \quad . \quad (32)$$

By equation (15), chapter IV, the volume common to a crystal and its 'ghost' shifted a distance t in the hkl direction is

$$V(t) = \iint (T - t) dy dz,$$

so

$$\begin{aligned} I(S) &= (2/U) \int_0^+ V(t) J(t) \cos (2\pi t u/a) dt \\ &\quad - (2/U) \int_0^+ V(t) K(t) \sin (2\pi t u/a) dt \\ &= (2/U) \int_0^+ V(t) J(t) \cos 2\pi s t dt \\ &\quad - (2/U) \int_0^+ V(t) K(t) \sin 2\pi s t dt \quad . \quad (33) \end{aligned}$$

where the integration extends to a large enough value of t for $V(t)$ to vanish, and $s = u/a$ is the actual distance by which S misses the point h, k, l of the reciprocal lattice. It will be remembered that u is the fraction of the distance $1/a$ between the reciprocal lattice points by which S misses the point of the reciprocal lattice. Since $J(t)$, $V(t)$ and $\cos 2\pi s t$ are unaffected by a change in the sign of t , and $K(t)$ and $\sin 2\pi s t$ both change sign, equation (33) may be written

$$\begin{aligned} I(S) &= U^{-1} [\int V(t) J(t) \cos 2\pi s t dt \\ &\quad - \int V(t) K(t) \sin 2\pi s t dt] \quad . \quad (34) \end{aligned}$$

where the limits of integration are the negative and positive values of t for which $V(t)$ vanishes. This equation is very similar to equation (21) of chapter IV, and in fact reduces to it if there are no mistakes, for then $J(t)$ is constant and $K(t)$ is zero.

Ordinarily $J(t)$ will have the form

$$J(t) = J_0 \exp (-\gamma |t|),$$

where γ is a function of h, k and l , and $K(t)$ will be zero. If mistakes are sufficiently frequent to cause line broadening $J(t)$ will become inappreciable before $V(t)$ departs

greatly from its value for $t = 0$. Equation (34) then becomes

$$I(S) = J_0 V U^{-1} \int_{-\infty}^{+\infty} \exp(-\gamma |t|) \cos 2\pi s t \, dt$$

$$= \frac{J_0 V}{U} \cdot \frac{2\gamma}{\gamma^2 + (2\pi s)^2} \quad (35)$$

The maximum value of this is $I_s = 2J_0 V/U\gamma$, so that the apparent particle size is

$$\varepsilon = I_s/I = 2/\gamma, \quad (36)$$

and the integral breadth is

$$\beta = \lambda/\varepsilon \cos \theta = \lambda\gamma/2 \cos \theta. \quad (37)$$

When $K(t)$ is not zero one may expect displacement as well as broadening of the lines.

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(References to experimental work on substances mentioned above will be found in the next chapter.)

CHAPTER VI

MISTAKES IN LAYER STRUCTURES : SILICATES, COBALT, GRAPHITE

MISTAKES IN THREE DIMENSIONS : POWDER PHOTOGRAPHS OF AuCu_3

1. THE mistake specially considered in paragraph 3 of the preceding chapter does not seem to occur, but a similar one with a shift of one-third or two-thirds of the b axis is found in some layer silicates (Hendricks, 1940). Suppose that the three types of layer are A , B , and C , and that the crystal starts off $AAA\cdots$, but that at each added layer there is a chance α of a mistake occurring, and the sequence continuing $BBB\cdots$ or $CCC\cdots$. Suppose, further, that either mistake is equally likely. Let the probability of the n^{th} added layer being A be A_n , of being B be B_n , and of being C be C_n .

Then
$$A_{n+1} = (1 - \alpha)A_n + \frac{1}{2}\alpha B_n + \frac{1}{2}\alpha C_n, \quad (1)$$

the factors of one-half coming in because, if the n^{th} added layer is B or C and a mistake occurs, the $(n+1)^{\text{th}}$ will be A only half the time. Since $A_n + B_n + C_n = 1$, equation 1 may be written

$$A_{n+1} = (1 - \frac{3}{2}\alpha)A_n + \frac{1}{2}\alpha. \quad (2)$$

This may be solved in the same way as equation 6 of the preceding chapter, the solution being

$$A_n = \frac{1}{3} + Q(1 - \frac{3}{2}\alpha)^n \quad (3)$$

where Q is an arbitrary constant. Similar equations can be set up for B_n and C_n , with the same solution. Choosing the constants so that $A_0 = 1$, $B_0 = C_0 = 0$, gives

$$\left. \begin{aligned} A_n &= \frac{1}{3}[1 + 2(1 - \frac{3}{2}\alpha)^n], \\ B_n &= \frac{1}{3}[1 - (1 - \frac{3}{2}\alpha)^n], \\ C_n &= \frac{1}{3}[1 - (1 - \frac{3}{2}\alpha)^n]. \end{aligned} \right\} \quad (4)$$

If the structure amplitude of the A plane is F , that for the

B plane will have an A part of $F \cos (2\pi k/3)$ and a B part of $F \sin (2\pi k/3)$, and that for the C plane will have an A part of $F \cos (4\pi k/3)$ and a B part of $F \sin (4\pi k/3)$. Finding the mean value of the product $AA' + BB'$ is simplified by the fact that $B = 0$, so that J_m is the mean value of AA' , and is given by

$$\begin{aligned} J_m &= F^2[A_m + B_m \cos (2\pi k/3) + C_m \cos (4\pi k/3)] \\ &= \frac{1}{3}F^2[\{1 + \cos (2\pi k/3) + \cos (4\pi k/3)\} \\ &\quad + (1 - \frac{3}{2}\alpha)^m \{2 - \cos (2\pi k/3) - \cos (4\pi k/3)\}] \\ &= F^2, \quad k = 3 \times \text{an integer}, \\ &= F^2(1 - \frac{3}{2}\alpha)^m, \quad k = (3 \times \text{an integer}) \pm 1. \end{aligned} \quad (5)$$

In deriving equation (5) it was tacitly assumed that one of the planes concerned was an A plane, but the same result is obtained if a B plane or a C plane is assumed. It is readily seen that K_m is zero :

$$\begin{aligned} K_m &= F^2[A_m \times 0 + B_m \sin (2\pi k/3) + C_m \sin (4\pi k/3)] \\ &= 0, \end{aligned}$$

since $B_m = C_m$ and $\sin (4\pi k/3) = -\sin (2\pi k/3)$.

Since $J_m = F^2$ the reflections with $k/3$ integral are unaffected, but those with $k/3$ fractional are drawn out into streaks in reciprocal space parallel to the c^* axis, the variation of intensity along the streaks being given by equation (23), chapter V :

$$\begin{aligned} I(w) &= \frac{2NF^2\gamma}{\gamma^2 + (2\pi w)^2}, \\ &= \frac{12NF^2\alpha}{9\alpha^2 + (4\pi w)^2} \quad (6) \end{aligned}$$

since $\gamma = 3\alpha/2$. On a rotating-crystal photograph these will show as streaks along curves in the photograph corresponding to lines parallel to the c^* axis, but on a powder photograph they will be somewhat fore-shortened, and lines for which OQ is perpendicular to c^* will be practically unbroadened. For example, in an orthogonal crystal the lines with $l = 0$ will be sharp, as well as those with k

divisible by three. A more extended discussion of the fore-shortening is given below, in connection with line-broadening in photographs of cobalt, and of the lines with $l = 0$, in connection with graphite. Hendricks (1940) has made an extensive investigation of silicates showing mistakes of this type, but has not attempted a quantitative comparison with theory.

The other mistake possible with the silicate minerals is an increase in the interlayer spacing at random intervals. If the mistake consists of an increase of the spacing by a fraction g , each mistake will cause an increase of the phase of all succeeding layers of $2\pi lg$. The mean value of the product $AA' + BB'$ for layers separated by m interlayer spaces will therefore be

$$\begin{aligned}
 J_m &= F^2 \text{ multiplied by the chance of no mistake in } m \text{ layers} \\
 &\quad + F^2 \cos 2\pi lg \text{ times the chance of one mistake in } m \text{ layers} \\
 &\quad + F^2 \cos 4\pi lg \text{ times the chance of two mistakes in } m \text{ layers} \\
 &\quad + \dots \\
 &\quad + F^2 \cos 2\pi mlg \text{ times the chance of } m \text{ mistakes in } m \text{ layers} \\
 &= F^2 \left[(1 - \alpha)^m + m\alpha(1 - \alpha)^{m-1} \cos 2\pi lg \right. \\
 &\quad \left. + \frac{m(m-1)}{2!} \alpha^2 (1 - \alpha)^{m-2} \cos 4\pi lg + \dots + \alpha^m \cos 2\pi mlg \right].
 \end{aligned}$$

In the problems so far considered K_m , the mean value of $AB' - A'B$, has been zero, a considerable simplification being thus produced. In the present case, however, K_m does not vanish, but is given by an expression like that for J_m , except that the cosines are replaced by sines, so that

$$\begin{aligned}
 K_m &= F^2 \left[m\alpha(1 - \alpha)^{m-1} \sin 2\pi lg \right. \\
 &\quad \left. + \frac{m(m-1)}{2!} \alpha^2 (1 - \alpha)^{m-2} \sin 4\pi lg + \dots + \alpha^m \sin 2\pi mlg \right].
 \end{aligned}$$

(The term in $(1 - \alpha)^m$ is missing in the expression for K_m because it is multiplied by the sine of zero, and so vanishes, whereas in J_m it is multiplied by the cosine of zero, which is unity.) With expressions as complicated as these for J_m and K_m it is not possible to evaluate equation (28), chapter V, simply by elementary means, and recourse must be had to methods involving complex quantities. It may be said, however, that K_m different from zero means that $w = 0$ is no longer the position of maximum intensity, so that we may expect a change in the positions of the reflections as well as a broadening.

2. In hexagonal cobalt the mistake is a shift of one-third in the a direction and two-thirds in the b direction, or else twice this (paragraph 2, chapter V). If the structure amplitude of an A plane is F , that for a B plane has an

A part of $F \cos 2\pi \left(\frac{h}{3} + \frac{2k}{3} \right) = F \cos 2\pi \left(\frac{h - k}{3} \right)$, and a B

part of $F \sin 2\pi \left(\frac{h}{3} + \frac{2k}{3} \right) = F \sin 2\pi \left(\frac{h - k}{3} \right)$, while that

of a C plane has an A part of $F \cos 2\pi \left(\frac{h - k}{3} \right)$ and a B part

of $-F \sin 2\pi \left(\frac{h - k}{3} \right)$. The problem differs from that

just treated in that the n^{th} layer and the $(n + 1)^{\text{th}}$ *must* be different; the mistake consists of the $(n + 2)^{\text{th}}$ being unlike the n^{th} . Thus if the first plane is A and the second B , the third ought to be A , but there is a chance α that it is C . Let A_n be the chance that the n^{th} added plane is like the first. The probability that the $(n + 2)^{\text{th}}$ is like the $(n + 1)^{\text{th}}$ is zero, that it is like the n^{th} is $(1 - \alpha)$, and that it is like neither is α , so

$$\begin{aligned} A_{n+2} &= (1 - \alpha)A_n + 0 \times A_{n+1} + \alpha(1 - A_n - A_{n+1}), \\ \text{or} \quad A_{n+2} + \alpha A_{n+1} - (1 - 2\alpha)A_n &= \alpha. \end{aligned} \quad (7)$$

This is a nastier equation than either (6), chapter V, or

(2), above, but it can be solved in the same way. Let

$$A_n = P + Q\rho^n,$$

$$P + Q\rho^{n+2} + \alpha P + \alpha Q\rho^{n+1} - (1 - 2\alpha)P - (1 - 2\alpha)Q\rho^n = \alpha,$$

$$P = 1/3,$$

$$\rho^{n+2} + \alpha\rho^{n+1} - (1 - 2\alpha)\rho^n = 0,$$

$$\rho = \frac{-\alpha \pm \sqrt{\alpha^2 + 4 - 8\alpha}}{2}. \quad (8)$$

It will be found that the positive sign leads to reflections that, with the ordinary hexagonal indices, have l even, and the negative sign to reflections that have l odd. Let

$$\left. \begin{aligned} \rho_e &= \frac{-\alpha + \sqrt{4 - 8\alpha + \alpha^2}}{2}, \\ \rho_o &= \frac{-\alpha - \sqrt{4 - 8\alpha + \alpha^2}}{2}. \end{aligned} \right\} \quad (9)$$

Then
$$A_n = \frac{1}{3} + Q_e \rho_e^n + Q_o \rho_o^n \quad (10)$$

where Q_e and Q_o are arbitrary constants. They must be chosen so that $A_0 = 1$, $A_1 = 0$; the values required are readily found to be

$$\left. \begin{aligned} Q_e &= (1 + 2\rho_o)/3(\rho_o - \rho_e), \\ Q_o &= (1 + 2\rho_e)/3(\rho_e - \rho_o). \end{aligned} \right\} \quad (11)$$

For $c/Z \ll \alpha \ll 1$ these reduce to

$$\left. \begin{aligned} \rho_e &= 1 - \frac{3}{2}\alpha \approx \exp(-3\alpha/2), & Q_e &= 1/6, \\ \rho_o &= -1 + \frac{1}{2}\alpha \approx -\exp(-\alpha/2), & Q_o &= 1/2. \end{aligned} \right\} \quad (12)$$

The values of B_n and C_n , the probabilities that the n^{th} added plane will be B or C , are given by equation (10) with the constants chosen to make $B_0 = C_0 = 0$, $B_1 = C_1 = 1/2$, since the first added plane is equally likely to be B or C . It is found that

$$B_n = C_n = \frac{1}{3} + R_e \rho_e^n + R_o \rho_o^n$$

where

$$\left. \begin{aligned} R_e &= (1 + 2\rho_o)/6(\rho_e - \rho_o) \doteq -1/12, \\ R_o &= (1 + 2\rho_e)/6(\rho_o - \rho_e) \doteq -1/4. \end{aligned} \right\} \quad (13)$$

The mean value of $AA' + BB'$ is then

$$\begin{aligned} J_m &= F^2 A_m + F^2 B_m \cos 2\pi \left(\frac{h-k}{3} \right) + F^2 C_m \cos 2\pi \left(\frac{h-k}{3} \right) \\ &= F^2 \left[\frac{1}{3}(1 + 2C) + (Q_e + 2CR_e)\rho_e^m \right. \\ &\quad \left. + (Q_o + 2CR_o)\rho_o^m \right] \quad (14) \end{aligned}$$

where C has been written for $\cos 2\pi \left(\frac{h-k}{3} \right)$. For $h-k$ divisible by three this reduces to F^2 ; for $h-k$ not divisible by three it reduces to

$$J_m \doteq F^2 \left(\frac{1}{4}\rho_e^m + \frac{3}{4}\rho_o^m \right)$$

$$\text{or } F^2 \left[\frac{1}{4} \exp(-3\alpha m/2) + \frac{3}{4} \cos m\pi \exp(-\alpha m/2) \right] \quad (15)$$

approximately. The value of K_m is readily found to be zero. Reflections with $h-k$ divisible by three are normal, since for them $J_m = F^2$; the line-profiles for the other reflections are given by

$$\begin{aligned} I(w) &= 2N \int_0^\infty J_m \cos 2\pi w m \, dm \\ &\doteq 2NF^2 \int_0^\infty \left\{ \frac{1}{4} \exp(-3\alpha m/2) \right. \\ &\quad \left. + \frac{3}{4} \exp(-\alpha m/2) \cos m\pi \right\} \cos 2\pi w m \, dm \\ &= 2NF^2 \left\{ \frac{1}{4} \frac{\frac{3\alpha}{2}}{\left(\frac{3\alpha}{2} \right)^2 + (2\pi w)^2} + \frac{3}{8} \frac{\frac{\alpha}{2}}{\left(\frac{\alpha}{2} \right)^2 + [2\pi(w + \frac{1}{2})]^2} \right. \\ &\quad \left. + \frac{3}{8} \frac{\frac{\alpha}{2}}{\left(\frac{\alpha}{2} \right)^2 + [2\pi(w - \frac{1}{2})]^2} \right\} \quad (16) \end{aligned}$$

(The second integration is done by expressing the product of two cosines as the sum of two cosines.) This is a rather more complex expression than we have obtained previously, but the interpretation is straightforward. The points of the reciprocal lattice have broad weak peaks of integral breadth $\sigma = 3\alpha/4$ and intensity $NF^2/4$, while halfway between them there are sharper stronger peaks of integral breadth $\sigma = \alpha/4$ and intensity $3NF^2/4$. The reason for this apparent halving of the reciprocal lattice is that we have been taking a unit cell as consisting of a single plane, whereas the normal unit cell of hexagonal cobalt consists of two planes. The reciprocal lattice, with the ordinary

values of l , is illustrated in figure 1. The points with $h - k$ divisible by three and l even are sharp, and with l odd are missing. The points with $h - k$ not divisible by three and l even are drawn out into long streaks parallel to the c^* axis; those with l odd are also drawn out, but only one-third as much. The integral breadths

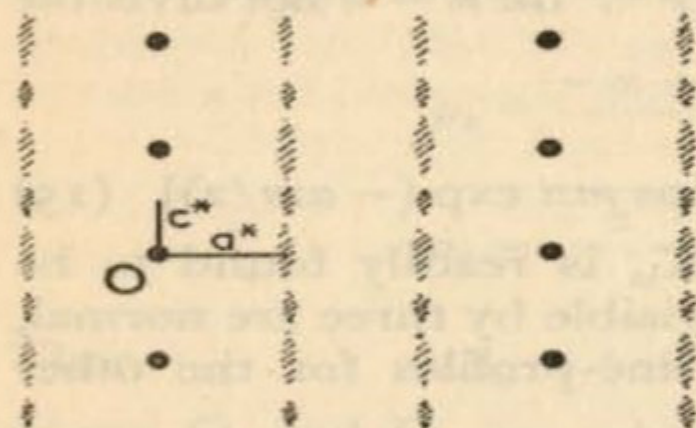


FIG. 1.—Portion of the reciprocal lattice for cobalt.

referred to the ordinary values of l are twice those given above, so that $\sigma = 3\alpha/2$ for reflections with l even, and $\sigma = \alpha/2$ for reflections with l odd.

In the case of cobalt the strict calculation of the intensity has been carried out, equation (26), chapter V, for the line-profile and equations (9), (11) and (13) for the ρ 's and Q 's being used. For α small compared with c/Z the reciprocal lattice for normal hexagonal close-packing is obtained, for α large compared with c/Z but small compared with one-half it is as just described, and for $\alpha \sim 1/2$ the fuzzy regions practically disappear. For α a little greater than one-half the ρ 's become imaginary, but $I(w)$ can still be interpreted, fuzzy regions appearing in places correspond-

ing to the points of the reciprocal lattice for cubic close-packing. As α approaches unity these regions coalesce into sharp points, the final state being the superposition of the reciprocal lattices for the two orientations of the cubic crystal corresponding to the sequences of planes $ABCABC\cdots$ and $ACBACB\cdots$. This is as it should be, since an hexagonal crystal with a mistake at every plane ($\alpha = 1$) would be cubic close-packed, but the beginnings AB and AC are equally likely.

A careful experimental study of the broadening of the X-ray reflections from imperfect hexagonal cobalt has been made by Edwards and Lipson (1942), both single-crystal and powder photographs being used. The single-crystal photographs showed in a striking manner the extension of the regions of reflection along lines parallel to the c^* axis, and the fact that reflections with l odd were much less affected than those with l even. They were, however, unsuitable for quantitative measurements, and for this purpose a powder photograph taken with crystal-reflected nickel radiation was used. (Crystal-reflected radiation

is practically monochromatic, consisting almost entirely of one doublet, and so gives photographs with less background than merely filtered radiation does.) The integral breadths were derived by the method of Jones (1938). The integral breadths are given in the second column of table I. They depend, however, on the actual value of l , as well as on α and the parity (oddness or evenness) of l . This is easily seen from figure 2.

A 'spike' of length in reciprocal space δ corresponds for $l = l_1$ to a range of $\sin \theta$ proportional to B_1C_1 , whereas for $l = l_2$ it corresponds to the greater range proportional

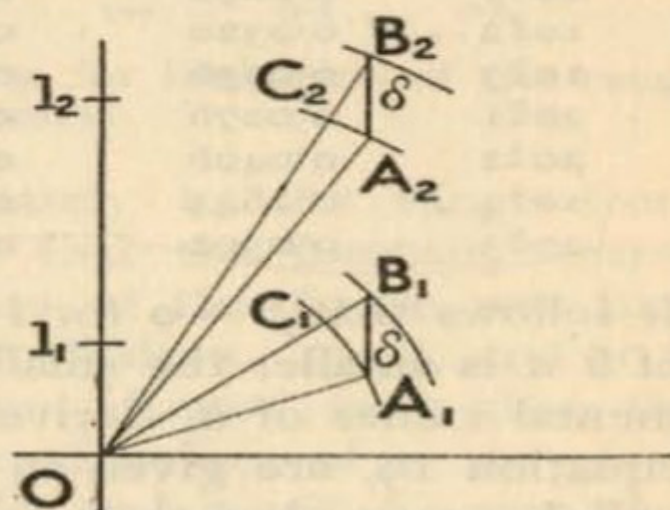


FIG. 2.—Dependence of the breadth of a reflection on l .

to B_2C_2 . The relation between β and l is most easily got from the equation

$$\sin^2 \theta = \lambda^2(h^2 + hk + k^2)/3a^2 + \lambda^2 l^2/4c^2, \quad (17)$$

which relates the angle of reflection to the indices of reflection for an hexagonal crystal. Differentiation gives

$$2 \sin \theta \cos \theta \frac{d\theta}{dl} = \frac{\lambda^2 l}{2c^2}. \quad (18)$$

If σ is the integral breadth in l , or w , which amounts to the same thing,

$$\beta = 2\sigma \frac{d\theta}{dl},$$

$$\sigma = \frac{1}{2}\beta \frac{dl}{d\theta} = \frac{c^2}{\lambda^2} \frac{\sin 2\theta}{l} \beta. \quad (19)$$

TABLE I

Calculation of α , the probability of a mistake per added plane of atoms, in a specimen of Cobalt

Line	β	σ	α	α corr.
10 $\bar{1}$ 1	0.0092	0.043	0.086	0.088
10 $\bar{1}$ 2	0.0320	0.089	0.059	0.073
10 $\bar{1}$ 3	0.0256	0.051	0.102	0.111
20 $\bar{2}$ 1	0.0076	0.044	0.088	0.093
20 $\bar{2}$ 2	0.0406	0.105	0.070	0.088
10 $\bar{1}$ 4	0.0844	0.099	0.066	0.119
20 $\bar{2}$ 3	0.0592	0.042	0.084	0.093

It follows that $\beta = 0$ for $l = 0$, and that for a given value of θ it is smaller the smaller the value of l . The experimental values of σ , derived from those of β by means of equation 19, are given in column three of the table. It will be seen that they fall into two groups, those with $\sigma \sim 0.045$ (l odd), and those with $\sigma \sim 0.10$ (l even). The theory given above predicts $\sigma = 3\alpha/2$ for the lines with l even, and $\sigma = \alpha/2$ for the lines with l odd. The value of α , the chance of a mistake per added plane, is thus about 0.090 if calculated from the lines with l odd, and about 0.067 if calculated from the lines with l even.

This is not entirely satisfactory agreement. Though the value of α is not very small compared with one-half, errors due to the various approximations made (for example, the use of equations (12) instead of (9) and (10)) do not seem sufficient to account for the discrepancy directly. A more probable explanation is limitation of the range of photometry. The theoretical profile of $I(w)$ is shown in figure 3. In calculating the integral breadth as $\sigma = \int I dw / I(0)$ it is tacitly assumed that it is possible to photometer a sufficient length on the film on each side of the line to get practically all the intensity. In the present case the region that it was possible to photo-

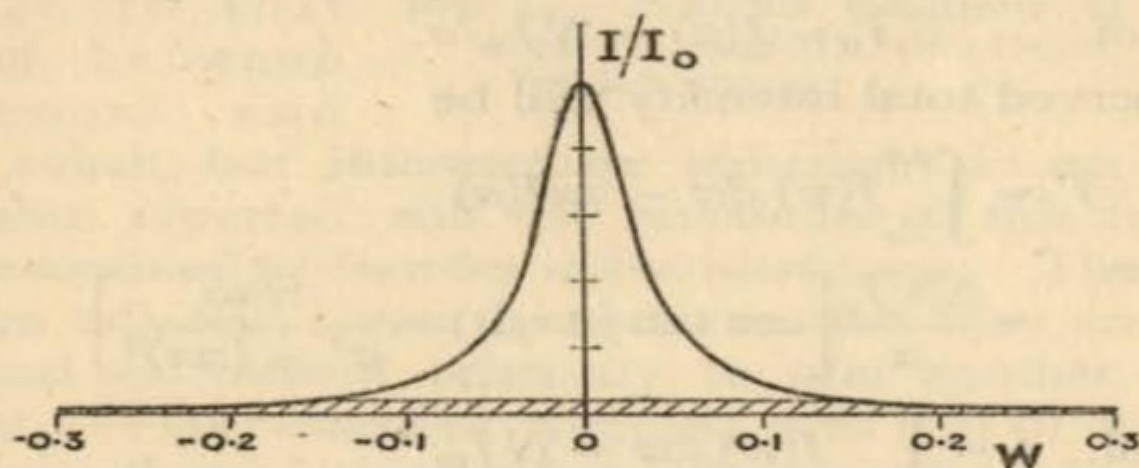


FIG. 3.—Correction of the intensity for limitation of the range of photometry.

meter corresponded approximately to the range from $w = -0.15$ to $w = +0.15$, so that the intensity corresponding to the shaded portion of the figure was lost. A correction can be calculated (Wilson, 1942), and it is found that lines with l even are affected more than the lines with l odd. The corrected values of α are given in the fifth column of the table, and it will be seen that the discrepancy has practically disappeared. The mean of the corrected values of α is 0.096 ± 0.008 from the odd lines and 0.093 ± 0.014 from the even lines. It seems, therefore, that the assumption of mistakes in the structure, distributed at random along the hexagonal axis, explains satisfactorily the broadening of the lines and accounts

quantitatively for the difference between the lines with different parity.

The correction to the breadths may be calculated as follows. If the integral breadth in w is σ ,

$$I(w) = \frac{NJ_0\sigma}{\sigma^2 + (\pi w)^2} \quad (20)$$

(equation 30, chapter V, with γ replaced by 2σ). If the range of photometry is from $w = -x$ to $w = +x$, the observed maximum intensity will be

$$\begin{aligned} I'_0 &= I(0) - I(x) \\ &= I_0\pi^2x^2/(\sigma^2 + \pi^2x^2) \end{aligned} \quad (21)$$

instead of $I_0 = I(0) = NJ_0/\sigma$. (22)

The observed total intensity will be

$$\begin{aligned} I' &= \int_{-x}^{+x} I(w) dw - 2xI(x) \\ &= \frac{2NJ_0}{\pi} \left[\arctan(\pi x/\sigma) - \frac{\pi x\sigma}{\sigma^2 + (\pi x)^2} \right] \end{aligned} \quad (23)$$

instead of $I = \int_{-\infty}^{+\infty} I(w) dw = NJ_0$. (24)

The observed integral breadth will therefore be

$$\sigma' = \frac{2\sigma}{\pi} \left[(1 + \sigma^2/\pi^2x^2) \arctan(\pi x/\sigma) - \sigma/\pi x \right], \quad (25)$$

instead of σ as it ought to be. For $x = 0.15$, $\sigma' = 0.045$ (mean for l odd) a little trial and error gives $\sigma = 0.051$, and for $\sigma' = 0.098$ (mean for l even) it gives $\sigma = 0.140$. The corresponding values of α are 0.102 and 0.093, in fair agreement with one another and with the values found by Wilson by correcting each line individually.

3. Another substance exhibiting mistakes is graphite, and it has been the subject of numerous investigations in connection with lamp black, coke, arc carbons and other commercially important products. The ideal graphite structure consists of layers like those shown in figure 4,

alternate layers taking the positions *A* and *B*. Well-crystallized graphite usually consists chiefly of this structure, but contains also an appreciable fraction of another structure in which the layer sequence is *ABCABC*...

(Lipson and Stokes, 1942). The relation between these structures is

similar to that existing between hexagonal and

cubic cobalt, but intermediate structures do not seem to have been reported, and the remainder of this discussion will be confined to disorder in the ideal form. The binding between adjacent layers is weak, so that they are readily displaced or rotated relatively to one another by any amount. This behaviour contrasts with that of cobalt and the layer silicates, which allow only a small number of different displacements. In addition, the crystals are small, so that it is necessary to consider 'particle size' broadening as well as 'mistake' broadening.

The structure of ordinary, non-ideal, graphite may be pictured as a sequence of planes *ABAB*... for a certain distance, but at each added plane there is a chance of a random translation and rotation, destroying completely the regular phase relation between atoms separated by the displacement. This will not affect the *ool* reflections, so that for them the intensity will depend on *w* through the ordinary factor

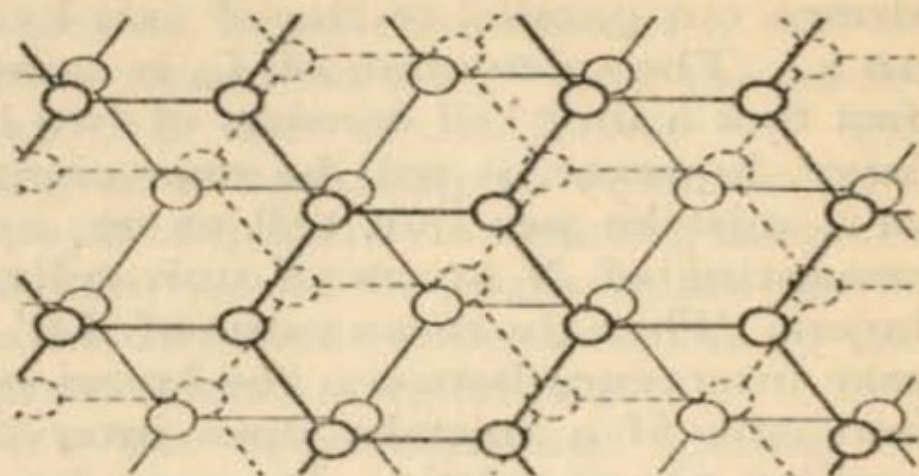


FIG. 4.—Possible positions of graphite layers, slightly displaced to show hidden atoms.

$$I(w) = F^2 \frac{\sin^2 \pi N w}{(\pi w)^2} \quad (26)$$

where N is the number of unit cells in the crystal in the c direction (chapter III), but all other reflections will be drawn out parallel to the c^* axis by an amount depending on α . The calculation of J_m is complicated slightly by the fact that a unit cell consists of two layers. If α is not too large, however, it will be near enough to take the chance of a mistake per unit cell as 2α , and treat the crystal as consisting of N layers of unit cells, instead of $2N$ actual layers. Then the mean value of $AA' + BB'$ is F^2 if no mistake intervenes between the layers of unit cells concerned, and zero if a mistake does intervene, since there is no regular phase relation between layers separated by mistakes. The value of J_m is therefore F^2 multiplied by the chance of there being no mistake in m added layers of unit cells, so

$$J_m = F^2(1 - 2\alpha)^m \doteq F^2 \exp(-2\alpha m). \quad (27)$$

The intensity of reflection for reflections other than the ool's will therefore depend on w through the factor

$$I(w) = \frac{N\alpha F^2}{\alpha^2 + (\pi w)^2} \quad (28)$$

(equation (24), chapter V). For α not too large a specimen consisting of such crystals will give ool powder lines as sharp as the length of the crystal in the c direction permits, and hkl lines with breadths depending on α and l through a relation similar to equation (19):

$$\beta = \frac{\lambda^2 l}{c^2 \sin 2\theta} \alpha, \quad (29)$$

the integral breadth in w of (28) being α .

The reciprocal lattice just described, consisting of relatively sharp points on the c^* axis, and all other reflections represented by streaks, suffices to treat powder photographs, but it is not strictly correct. The regions separated by mistakes are not only translated with respect to one

another, but are also rotated by random amounts. This corresponds to a rotation of the reciprocal lattice about the c^* axis, so that the reflections, other than the ool's, will be turned into cylinders with centres on the c^* axis, the intensity being uniform around the circumference of the cylinders, but depending on w according to equation (28). A single-crystal photograph of graphite containing mistakes of the sort considered here would be expected to show, therefore, broad bands in directions perpendicular to the c^* axis, rather than narrow streaks parallel to it.

For large values of α the approximations leading to equations (28) and (29) are no longer valid, and further consideration is needed. It does not seem worth while to treat intermediate cases, but the final state of a shift at every added plane ($\alpha = 1$) is of importance. The ool reflections will be, as before, relatively sharp points depending on w according to equation (26), but the other reflections will be joined up into continuous lines parallel to c , and of intensity uniform in w except for the falling off of the atomic scattering factor with increasing $\sin \theta/\lambda$. The crystal behaves essentially as if it were single for the ool reflections, giving points as sharp as its size allows, but as an assemblage of non-co-operating planes for all other reflections, giving lines in reciprocal space perpendicular to the planes (chapter II, paragraph 4). Crystals as faulty as this will not be large enough to give single-crystal photographs, so that the rotation of the reciprocal lattice, producing cylinders instead of lines, need not be considered.

A powder photograph of a specimen consisting of such crystals will show lines of two types. Lines of the first type correspond to the ool reflections, and are essentially similar to the broadened lines considered in chapter IV. The apparent particle size may be got from equation (26), but it is perhaps instructive to use the method of chapter IV. For this purpose the crystal may be considered a cylinder (not necessarily circular) of length Z , so that $V(t)$, for a shift parallel to the c axis, is $P(Z - |t|)$, where

differ from any so far encountered. The calculation of the line profiles involves mathematical functions beyond the scope of this book, so we must content ourselves with a qualitative treatment. As we have seen, through every lattice point (h, k) in the plane $l = 0$ there passes a rod-like region of reflection. The intensity on the film with θ between θ and $\theta + d\theta$ will depend on the amount of this rod that lies between concentric spheres of radii S and $S + dS$, where $dS = 2 \cos \theta d\theta / \lambda$ (figure 5). The radius of the rod is of the order of $1/2p$, where p is the square root of the area of a layer. Let s be the amount by which

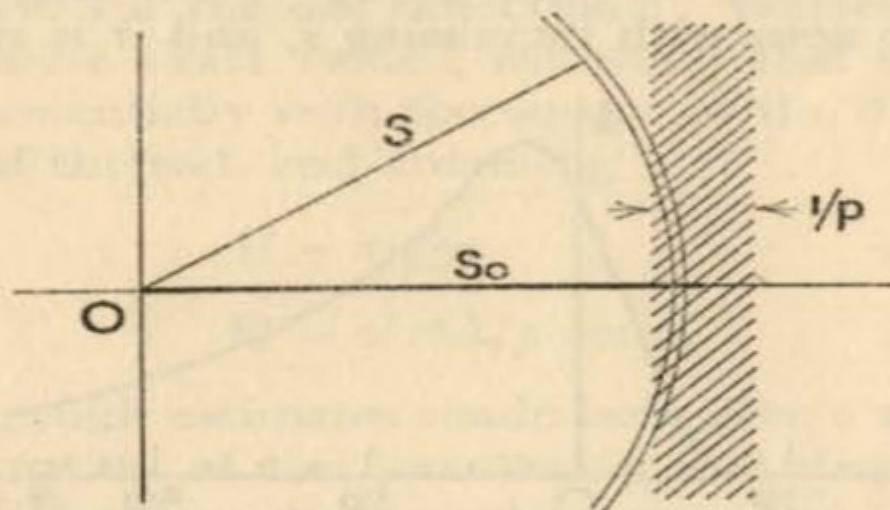


FIG. 5.—Calculation of the line profile for hkl reflections.

S differs from its value S_0 at the point hko . The intensity due to the rod will be zero until S is approximately $S_0 - 1/2p$, when it will increase rapidly until $S = S_0$. For $S > S_0$ the volume of the rod intercepted by the spheres continues to increase until S is approximately $S_0 + 1/2p$. Beyond this point it decreases again, but less rapidly than it initially increased. For $S > S_0$ the intensity on the film will at first continue to increase with the increasing volume intercepted by the spheres, but will not do so right up to $S_0 + 1/2p$, because the intensity in the rod is greatest in the middle and falls off at the outside. The maximum on the film will therefore lie somewhere between the value of θ corresponding to $S = S_0$ and that corresponding to

$S = S_0 + 1/2p$, or at about $S_0 + 1/4p$, say. The peak of the reflection is therefore displaced from the position where it would be expected by

$$\Delta\theta = (\lambda/2 \cos \theta)(1/4p) = 0.125 \lambda/p \cos \theta. \quad (35)$$

This displacement was discovered experimentally before the peculiar nature of the reflections was realized, and was interpreted as a contraction of the lattice in small crystals of graphite.

The approximate line profile as a function of s is shown in figure 6. The concept of integral breadth is not useful for dealing with such reflections, as the intensity never falls quite to zero with increasing s , and it is necessary to

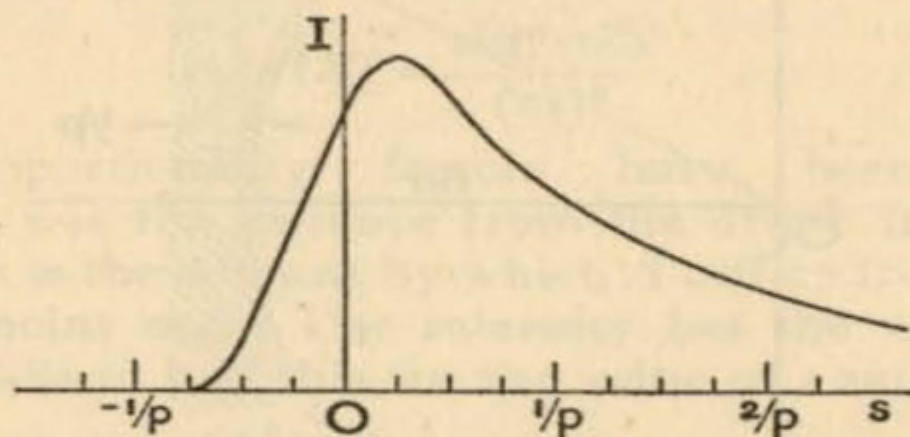


FIG. 6.—Approximate line profile for hkl reflections.

use the half breadth as a measure of the broadness of the reflection. The intensity reaches its maximum for $s \sim 1/4p$, but from the volumes intercepted by the spheres in the two positions it is pretty clear that the intensity for $s = 0$ is greater than half that for $s = 1/4p$. At a guess we might say that the intensity is half the maximum at the same distance to the other side of $s = 0$, or at $s = -1/4p$. The distance on the low-angle side between the maximum and the half value is thus $1/2p$. On the high-angle side there is nothing to aid in the estimation of the distance it is necessary to go to reach the half value, but as the rise in intensity is steeper than the fall it will certainly be more than on the low-angle side, and as a guess

we might double it and say $1/p$. The total half breadth in s of the reflection would then be $3/2p$, and the half breadth in 2θ would be

$$\beta' = (\lambda/\cos \theta)(3/2p) = 1.5\lambda/p \cos \theta, \quad (36)$$

and the apparent particle size calculated from the half breadth would be

$$\varepsilon' = \lambda/\beta' \cos \theta = 0.67p. \quad (37)$$

If our estimates are anywhere near right, therefore, the numerical factor is considerably different from the 1.13 derived above for the $00l$ reflections. Warren (1942) has calculated more exact values, assuming that the intensity falls off exponentially with the square of the distance from the centre of the rod, and obtaining

$$\varepsilon' = 0.57p \quad (38)$$

and
$$\Delta\theta = 0.16\lambda/p \cos \theta, \quad (39)$$

so that the rough estimates made here give a semi-quantitative explanation of the broadening and displacement of the lines. The apparent particle size can be estimated from both the apparent particle size and the displacement.

4. Line broadening due to three-dimensional mistakes in AuCu_3 has been extensively investigated by Jones and Sykes (Sykes and Jones, 1936; Jones and Sykes, 1938), who have measured the apparent particle size for various reflections. These are given for a typical specimen in table II, most of the entries being average values from four or five photographs. It will be seen that ε varies markedly with h , k and l , the extreme values, those for 100 and 110, differing by a factor of two. The reason for the broadening is fairly clearly the fact that the type of ordering is not the same throughout each single crystal, but 'changes step' occasionally, so that the probability of two cells separated by a distance t in the hkl direction being the same decreases with increasing t . The boundary between

regions of different types of order must be plane, as it would otherwise be unstable (Bragg, 1940), but there is no other general restriction on the mode of occurrence of mistakes. Wilson (1943) has considered five different possibilities:

- (i) mistakes occurring on any plane, whatever its inclination to the crystal axes,
- (ii) mistakes occurring only on planes perpendicular to the edges of the unit cube ($\langle 100 \rangle$ planes),
- (iii) mistakes occurring only on planes perpendicular to a face diagonal of the unit cube ($\langle 110 \rangle$ planes),
- (iv) mistakes occurring only on planes perpendicular to the body diagonal of the unit cube ($\langle 111 \rangle$ planes), and
- (v) mistakes occurring in such a way that gold atoms do not come into contact.

The fifth of these resembles the second in some ways, as a little consideration shows that it is only on planes perpendicular to the cube edges that mistakes can occur with-

TABLE II

Observed and calculated apparent particle sizes in a specimen of $AuCu_3$

Line	$\epsilon_{obs.}$	$\epsilon_{calc.}$	% error
100	200A	203A	+ 1.5
110	100	109	+ 9.0
210	120	131	+ 9.2
211	142	135	- 5.2
221	115	112	- 2.6
310	122	114	- 6.6
320	150	152	+ 1.2
321	124	122	- 1.6
410 + 322	128	127	- 0.8
411	161	157	- 2.5
421	115	112	- 2.6

out bringing gold atoms into contact, but there is an added restriction. If, for example, the order is of type *A*, and a mistake occurs on a plane perpendicular to the *a* axis, on the second hypothesis the order could change to *B* or

C or D , while on the fifth it could change only to D . The complete list of mistakes possible without bringing gold atoms into contact is

on planes perpendicular to the a axis, $A \rightleftharpoons D$, $B \rightleftharpoons C$,
on planes perpendicular to the b axis, $B \rightleftharpoons D$, $A \rightleftharpoons C$, and
on planes perpendicular to the c axis, $C \rightleftharpoons D$, $A \rightleftharpoons B$.

Values of $J(t)$ for each of these modes of occurrence of mistakes can be worked out by methods similar to those already employed for layer structures, but slightly more complex, because of the three-dimensional nature of the mistakes. If h , k and l are all even or all odd

$$J(t) = (Au + 3Cu)^2,$$

where Au and Cu are the scattering factors of the gold and copper atoms respectively. These are the reflections common to the ordered and the disordered state, and are sharp, in agreement with experiment, since $J(t)$ is constant. If h , k and l are not all even or all odd the five possibilities of occurrence of mistakes lead respectively to the following values of $J(t)$ and ε :

Variety of Mistake	$J(t)$	Apparent Particle Size
(i)	$(Au - Cu)^2 \exp\{-4\alpha t /3a\}$	$3a/2\alpha$
(ii)	$(Au - Cu)^2 \exp\{-4\alpha h t /3\sqrt{Na}\}$	$3\sqrt{Na}/2\alpha h$
(iii)	$(Au - Cu)^2 \exp\{-4\alpha(h+k) t /3\sqrt{(2N)a}\}$	$3\sqrt{(2N)a}/2\alpha(h+k)$
(iv)	$(Au - Cu)^2 \exp\{-4\alpha(h+k+l) t /3\sqrt{(3N)a}\}$	$3\sqrt{(3N)a}/2\alpha(h+k+l)$
(v)	$(Au - Cu)^2 \exp\{-2\alpha(p+q) t /\sqrt{Na}\}$	$\sqrt{Na}/\alpha(p+q)$

where h , k , l are the positive values of the indices arranged in the order $h > k > l$, $N = h^2 + k^2 + l^2$, α is the chance of a mistake occurring in a distance equal to a (the edge of the unit cell), and p and q are the indices of the same parity (that is, the two that are even, or the two that are odd, as the case may be). It is not possible to choose α so that any of these expressions gives quantitative agreement with the experimental values reproduced in table II, but the fifth comes close to it. The chief discrepancy is the 100 reflection, for which the theoretical value of ε is $a/\alpha(0+0) = \infty$, so that the reflection should be sharp. It is actually the sharpest of the broadened reflections,

which suggests that a combination of two varieties of mistake, the fifth which gives good qualitative agreement, and the first to give a general fuzziness independent of indices, would give quantitative agreement. For this combination it is found that

$$(vi) \quad J(t) = (Au - Cu)^2 \exp \left\{ - [2\alpha'(p + q)/\sqrt{N} + 4\alpha''/3](|t|/a) \right\}, \quad (40)$$

where α' and α'' are the probabilities of the two kinds of mistake. This equation gives

$$\varepsilon = \frac{1}{\frac{\alpha'(p + q)}{\sqrt{Na}} + \frac{2\alpha''}{3a}} \quad (41)$$

With this expression for ε it is possible to get fair quantitative agreement with the experimental values. Apparent particle sizes calculated with $\alpha'/a = 0.00303$ and $2\alpha''/3a = 0.00492$ are given in column three of table II, and it will be seen that the greatest difference between the observed and calculated values is less than 10 per cent. This agreement is very satisfactory, the difficulties of measuring line breadths being considered, but it does not seem impossible that some other mode of occurrence of mistakes would give even better agreement.

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CHAPTER VII

THE USE OF COMPLEX QUANTITIES

1. IN the earlier part of this book an attempt has been made to keep the necessary mathematics as simple as possible, but a stage has now been reached where it seems desirable to introduce complex quantities. It is possible to proceed a little further without making explicit use of them, but already in the discussion of crystals with mistakes it has been necessary to postpone one or two topics because elementary methods became very clumsy, and clumsiness is evident from the first in any attempt to discuss diffraction by distorted crystals. It is, of course, impossible to give an adequate discussion of the nature and properties of complex quantities in the space available, but it is convenient to summarize the properties that will be used in the following chapters, and incidentally to clear up the difficulties postponed from chapters V and VI.

A complex quantity is of the form

$$z = x + iy, \quad (I)$$

where $i^2 = -1$ and x and y are ordinary numbers or variables. It is usual to call x the *real part* of z and y the *imaginary part*. A complex quantity may be represented in a plane by a line drawn from the origin of length equal to r , the positive value of $\sqrt{(x^2 + y^2)}$, and making an angle θ with the horizontal axis, where $r \cos \theta = x$, $r \sin \theta = y$. Since

$$\begin{aligned}\exp(i\theta) &= 1 + i\theta - \theta^2/2! - i\theta^3/3! + \theta^4/4! + i\theta^5/5! - \dots \\ &= 1 - \theta^2/2! + \theta^4/4! - \dots + i(\theta - \theta^3/3! + \theta^5/5! - \dots) \\ &= \cos \theta + i \sin \theta, \quad . \quad . \quad . \quad . \quad . \quad (2)\end{aligned}$$

a complex quantity may be written

$$\begin{aligned} z &= x + iy \\ &= r \cos \theta + ir \sin \theta \\ &= r \exp(i\theta). \end{aligned} \quad (3)$$

The sum of two complex quantities z_1 and z_2 is

$$z_1 + z_2 = x_1 + iy_1 + x_2 + iy_2 = x_1 + x_2 + i(y_1 + y_2), \quad (4)$$

and their product is

$$\begin{aligned} z_1 z_2 &= (x_1 + iy_1)(x_2 + iy_2) \\ &= (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + x_2 y_1). \end{aligned} \quad (5)$$

The product may be written more neatly in terms of r and θ , for

$$\begin{aligned} z_1 z_2 &= r_1 \exp(i\theta_1) \cdot r_2 \exp(i\theta_2) \\ &= r_1 r_2 \exp\{i(\theta_1 + \theta_2)\}. \end{aligned} \quad (6)$$

If the sign of i is changed wherever it occurs in a complex expression, the result is called the *conjugate* of the original expression. It is usually represented by the same letter with an asterisk affixed, so that if $z = x + iy$,

$$z^* = x - iy. \quad (7)$$

A quantity multiplied by its conjugate is purely real, and equal to the square of its absolute magnitude, for

$$zz^* = (x + iy)(x - iy) = x^2 + y^2 = r^2. \quad (8)$$

The relations between z , x , y , r , θ and z^* are shown

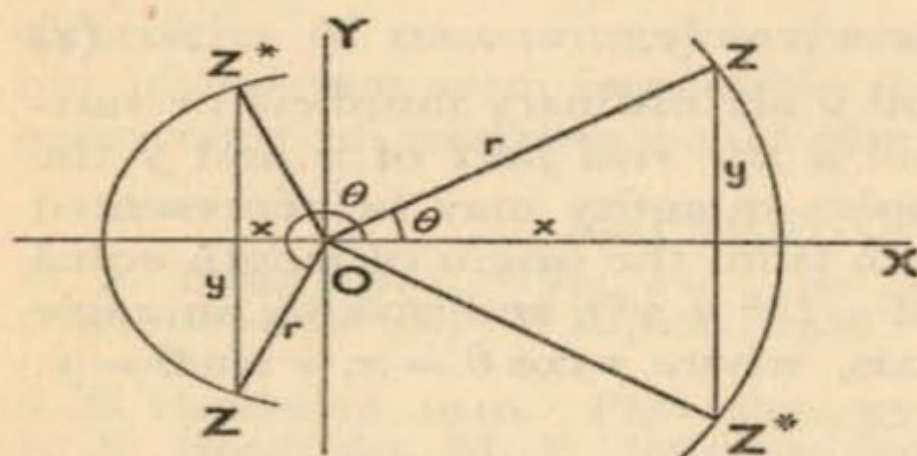


FIG. 1.—Representation of complex quantities.

diagrammatically in figure 1 for two values of z . In forming the conjugate of a complex expression it is not necessary to reduce it to the form $x + iy$ first. For instance, the conjugate of $(A - iB)/(C + iD)$ is $(A + iB)/(C - iD)$.

2. These properties

of complex quantities make possible a compact expression for the amplitude scattered by a unit cell. This is represented both in amplitude and phase by

$$F = \sum f_j \exp \{2\pi i(hx_j + ky_j + lz_j)\} \quad (9)$$

where f_j is the scattering factor and x_j, y_j, z_j are the co-ordinates of the j^{th} atom in the unit cell, and \sum_j means that the expression is to be summed for all atoms in the unit cell. It is easily verified that the real part of this is equal to A and the imaginary part to B (chapter V, paragraph 1).

2. In the calculation of the scattering factor from various imperfect structures it is necessary to calculate the mean value J of $AA' + BB'$ and K of $AB' - A'B$, where A, B and A', B' are the A and B parts of the structure amplitudes of two unit cells with a certain separation in the crystal. If $F = A + iB$, $F' = A' + iB'$,

$$\begin{aligned} FF'^* &= (A + iB)(A' - iB') \\ &= (AA' + BB') - i(AB' - A'B). \end{aligned} \quad (10)$$

Thus J is the mean value of the real part of FF'^* and $-K$ is the mean value of the imaginary part. It is often convenient to represent $J - iK$ by the single letter Y .

3. It is therefore important to calculate the mean value of expressions like $\exp(2\pi iux)$, where u is fixed and x is some variable quantity, such as one of the co-ordinates of position within a crystal, or the displacement of a unit cell from its mean position. When x varies over a small range of values on either side of zero, an approximate mean value can be obtained by expanding the exponential in a power series:

$$\exp(2\pi iux) = 1 + 2\pi iux - 2\pi^2 u^2 x^2 - 4\pi^3 i u^3 x^3 / 3 + \dots$$

If positive and negative values of x are equally frequent, the mean values of x, x^3 and other odd powers of x will be zero, and

$$\langle \exp(2\pi iux) \rangle = 1 - 2\pi^2 u^2 \langle x^2 \rangle + 2\pi^4 u^4 \langle x^4 \rangle / 3 - \dots,$$

where the angle brackets indicate average values. Now

$$\exp(-2\pi^2 u^2 \langle x^2 \rangle) = 1 - 2\pi^2 u^2 \langle x^2 \rangle + 2\pi^4 u^4 \langle x^2 \rangle^2 - \dots,$$

so that, if the difference between $\langle x^4 \rangle / 3$ and $\langle x^2 \rangle^2$ can be ignored,

$$\langle \exp(2\pi iux) \rangle = \exp(-2\pi^2 u^2 \langle x^2 \rangle).$$

In certain cases this approximation is exact, but it is always fairly good for small values of x .

4. If the probability of x having any particular value is given by $f(x)$, where the integral of $f(x)$ from $-\infty$ to $+\infty$ is unity, the mean value of $\exp(2\pi i u x)$ is given by the integral

$$\langle \exp(2\pi i u x) \rangle = \int_{-\infty}^{+\infty} f(x) \exp(2\pi i u x) dx,$$

which will of course depend on u . For the present, however, let us forget about the interpretation of this expression as an average, and consider the function $g(u)$ related to $f(x)$ by

$$g(u) = \int f(x) \exp(2\pi i u x) dx, \quad . \quad . \quad (11)$$

where the limits are understood to be $-\infty$ to $+\infty$ and $f(x)$ is any function of x for which the integral exists, and does not necessarily fulfil the condition that $\int f(x) dx = 1$. The function $g(u)$ so defined is called the *Fourier transform* of $f(x)$. It has the curious property that

$$f(x) = \int g(u) \exp(-2\pi i x u) du. \quad . \quad . \quad (12)$$

Except for a change in the sign of i , $f(x)$ is also the Fourier transform of $g(u)$. If both f and g are purely real they are Fourier transforms of one another, without this slight lack of symmetry in the relation. There have been numerous examples of somewhat-disguised Fourier transforms in earlier chapters; for example, the amplitude of reflection from a small crystal (chapter III, paragraph 6) is the three-dimensional Fourier transform of a function with value unity inside the crystal and value zero outside, and the intensity of reflection from a layer structure with mistakes (chapter V, equation (29)) is the transform of $J_m - iK_m$.

5. A rigorous proof of the relation expressed by equation (12) is difficult, but depends on the following argument. From the definition

$$g(u) = \int f(t) \exp(2\pi i u t) dt, \quad . \quad . \quad (13)$$

since the substitution of t for x as the variable of integration

makes no difference. Let

$$F(x) = \int g(u) \exp(-2\pi i x u) du. \quad (14)$$

Then

$$F(x) = \int [\int f(t) \exp(2\pi i u t) dt] \exp(-2\pi i x u) du,$$

or, on changing the order of integration,

$$F(x) = \int [\int \exp\{2\pi i(t-x)u\} du] f(t) dt. \quad (15)$$

The inner integral, $\int \exp\{2\pi i(t-x)u\} du$, is very peculiar. If $t = x$ it has the value infinity, since $\exp(0)$ is unity, whereas if $t \neq x$ $\exp\{2\pi i(t-x)u\}$ continually oscillates, but has the average value zero. The inner integral is thus zero if $t \neq x$, but at $t = x$ it has an infinitely high and infinitely narrow peak. In the integration with respect to t , therefore, the only region contributing anything will be an infinitely narrow strip containing the point $t = x$, and $F(x)$ will be equal to $f(x)$ multiplied by the area under the peak. In various ways this can be shown to be unity, so that

$$F(x) = f(x) \quad (16)$$

The difficulties over which much trouble has to be taken are first, justifying the change in the order of integration, and secondly, showing that the area of the peak is actually unity. One method of approach is to consider

$$F(x, \lambda) = \int g(u) \exp(-\lambda u^2 - 2\pi i x u) du \quad (17)$$

instead of $F(x)$, and to show that $F(x, \lambda)$ tends to $f(x)$ as λ tends to zero.

6. Let us now return to the problem of the scattering of X-rays from an imperfect crystal. The rays scattered by the unit cell at the point $n_1 a, n_2 b, n_3 c$ (the n^{th} unit cell, for short) are advanced in phase with respect to those scattered by the cell at the origin by

$$\delta_n = 2\pi(n_1 u + n_2 v + n_3 w) \quad (18)$$

where u, v, w are the co-ordinates of Q with respect to one of the points of the reciprocal lattice (chapter III, paragraphs 1, 6). If F_n is the value of the structure amplitude (9) for the n^{th} unit cell, the amplitude scattered by the

whole crystal will be

$$G(u, v, w) = \sum_n F_n \exp(i\delta_n), \quad (19)$$

where \sum_n means that the expression is to be summed for all unit cells. The intensity scattered will be given by equation (19) multiplied by its complex conjugate, so that

$$\begin{aligned} H(u, v, w) &= \sum_n \sum_{n'} F_n F_{n'}^* \exp \{i(\delta_n - \delta_{n'})\} \\ &= \sum_n \sum_{n'} F_n F_{n'}^* \exp \{2\pi i [u(n_1 - n'_1) + v(n_2 - n'_2) \\ &\quad + w(n_3 - n'_3)]\}. \end{aligned} \quad (20)$$

Note that in calculating H it is necessary to sum for all unit cells separately in G and G^* ;

$$I = \sum_n F_n F_n^* \exp \{i(\delta_n - \delta_n)\} = \sum_n |F_n|^2 \quad (21)$$

is something quite different from H , since it is independent of u, v, w . It is in fact the total intensity scattered by the crystal in the hkl direction, or the integral of H over one unit cell of reciprocal space.

In order to obtain from (20) an equation suitable for the actual calculation of H , it is necessary to get rid of the separate values of F for each unit cell, which are not known individually, and replace them by some sort of average values, which can be calculated in ways similar to those used for layer structures. Clearly the average must be taken in such a way that the exponential factor in equation (20) is not changed, or in other words, $F_n F_{n'}^*$ must be averaged for all values of n and n' that give the same values of $n_1 - n'_1, n_2 - n'_2, n_3 - n'_3$. In equation (20) let

$$n'_1 = n_1 + m_1, n'_2 = n_2 + m_2, n'_3 = n_3 + m_3, \quad (22)$$

so that

$$\begin{aligned} H(u, v, w) &= \sum_n \sum_m F_n F_{n+m}^* \exp \{-2\pi i(m_1 u + m_2 v + m_3 w)\} \\ &= \sum_n [\sum_m F_n F_{n+m}^*] \exp \{-2\pi i(m_1 u + m_2 v + m_3 w)\}, \end{aligned} \quad (23)$$

proper attention being paid to the limits of the summations.

What does the sum in brackets mean? Starting with any cell, designated by the numbers n_1, n_2, n_3 , we are to find the cell m_1a away in the direction of the a axis, m_2b away in the direction of the b axis, and m_3c away in the direction of the c axis, then multiply the structure amplitude of the first cell by the conjugate of the structure amplitude of the second, and add for all possible unit cells. For how many cells is it possible? At first one might answer: for every cell in the crystal, but actually this is true only for $m_1 = m_2 = m_3 = 0$. For $m_1 = 1$, for example, a layer of cells all over one side of the crystal must be omitted, as there are no cells at a distance a away in the direction of the a axis. For $m_1 = 10$, a layer ten cells thick must be omitted. Consideration shows that in general the number of cells to be included in the summation is the number common to the crystal and its 'ghost' shifted a distance m_1a in the direction of the a axis, m_2b in the direction of the b axis, and m_3c in the direction of the c axis. If this volume is called V_m , the number of cells to be included is V_m/U , where U is the volume of one unit cell. If, further, Y_m is the average value of the product $F_n F_{n+m}^*$ for all unit cells related by the displacement m_1a, m_2b, m_3c , then equation (23) becomes

$$H(u, v, w) = U^{-1} \sum_m V_m Y_m \exp \{ -2\pi i(m_1u + m_2v + m_3w) \}. \quad (24)$$

This is the general expression for the intensity of reflection as a function of position in reciprocal space for a crystal whose unit cells are not all alike, and is the solution of the problem postponed in chapter V, paragraph 9. It is clear that V_m is a generalization of the $V(t)$ used in chapter IV, and Y_m of $J_m - iK_m$, where J_m and K_m are the functions defined in chapter V. From the definitions it follows that changing the signs of the m 's leaves V_m unchanged, but turns Y_m into its conjugate. A little care is necessary, therefore, in carrying out calculations, as the algebraic expressions for V_m and Y_m do not always take account of these properties automatically.

The summation over m in equation (24) is to be done for all values of m_1, m_2, m_3 for which the product to be summed exists. Since the sign of the non-existence of the product is the vanishing of V_m , we may write the limits symbolically as $\pm \infty$ for each of the m 's, remembering to stop the summation when V_m vanishes. If, u, v, w are not too big, and Y_m is a 'smooth' function of the m 's, the summations in equation (24) may be replaced by integrations, giving

$$H(u, v, w) = (Uabc)^{-1} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} V(x, y, z) Y(x, y, z) \exp \{ - 2\pi i (ux/a + vy/b + wz/c) \} dx dy dz, \quad (25)$$

where $x = m_1 a, y = m_2 b, z = m_3 c$, and $V(x, y, z), Y(x, y, z)$ are V_m, Y_m with the appropriate substitutions. In a crystal containing mistakes $Y(x, y, z)$ may decrease so rapidly that the variation of $V(x, y, z)$ can be ignored, and the intensity written

$$H(u, v, w) = (Uabc)^{-1} V \iiint Y(x, y, z) \exp \{ - 2\pi i (ux/a + vy/b + wz/c) \} dx dy dz. \quad (26)$$

For a crystal without mistakes $Y(x, y, z)$ is a constant, equal to F^2 , and the intensity becomes

$$H(u, v, w) = (Uabc)^{-1} F^2 \iiint V(x, y, z) \exp \{ - 2\pi i (ux/a + vy/b + wz/c) \} dx dy dz, \quad (27)$$

giving an expression alternative to equations (15)–(17) of chapter III. It is easy to verify that equation (27) gives the same results in particular cases as were obtained by elementary means. For instance, for a parallelepiped of edges X, Y, Z ,

$$V(x, y, z) = (U/abc)(X - |x|)(Y - |y|)(Z - |z|), \quad (28)$$

and equation (27) gives on integration

$$H(u, v, w) = F^2 \cdot \frac{\sin^2 (\pi u X/a)}{(\pi u)^2} \cdot \frac{\sin^2 (\pi v Y/b)}{(\pi v)^2} \cdot \frac{\sin^2 (\pi w Z/c)}{(\pi w)^2}, \quad (29)$$

in agreement with chapter III, equation (7).

7. Equation (26) may be used to discuss the intensity of reflection from a structure with a variable interlayer spacing, postponed from chapter VI. The values of J_m and K_m found there (end of paragraph 1) give

$$\begin{aligned} Y_m &= J_m - iK_m \\ &= F^2[(1 - \alpha)^m + m\alpha(1 - \alpha)^{m-1} \exp(-2\pi ilg) \\ &\quad + \frac{m(m-1)}{2!} \alpha^2(1 - \alpha)^{m-2} \exp(-2\pi i \cdot 2lg) \\ &\quad + \cdots + \alpha^m \exp(-2\pi imlg)] \\ &= F^2[1 - \alpha + \alpha \exp(-2\pi ilg)]^m \end{aligned} \quad (30)$$

by the binomial theorem. The m in this equation is what would be called m_3 in the notation of the present chapter; since Y_m depends only on m_3 and not on m_1 and m_2 , $H(u, v, w)$ drops rapidly to zero very rapidly with u and w . If α is small $1 - \alpha[1 - \exp(-2\pi ilg)]$ is approximately equal to $\exp\{-\alpha[1 - \exp(-2\pi ilg)]\}$, so that

$$\begin{aligned} Y_m &\doteq F^2 \exp\{-m_3 \alpha[1 - \exp(-2\pi ilg)]\}, \\ Y(z) &= F^2 \exp\{-\alpha[1 - \exp(-2\pi ilg)]z/c\}. \end{aligned} \quad (31)$$

Equation (26) for the intensity of reflection as a function of u, v, w reduces to

$$H(w) = (V/U) \int_{-\infty}^{+\infty} Y(z) \exp(-2\pi i w z/c) d(z/c), \quad (32)$$

or, since $Y(-z) = Y^*(z)$ (page 91) and $V/U = N$,

$$\begin{aligned} H(w) &= NF^2 \left[\int_0^\infty \exp\{[-2\pi i w - \alpha\{1 - \exp(-2\pi ilg)\}]z/c\} d(z/c) \right. \\ &\quad \left. + \text{complex conjugate} \right] \\ &= NF^2 [\{\alpha[1 - \exp(-2\pi ilg)] + 2\pi i w\}^{-1} \\ &\quad + \text{complex conjugate}] \\ &= NF^2 [\{\alpha(1 - \cos 2\pi lg) + i(2\pi w + \alpha \sin 2\pi lg)\}^{-1} \\ &\quad + \text{complex conjugate}] \\ &= NF^2 \frac{2\alpha(1 - \cos 2\pi lg)}{\alpha^2(1 - \cos 2\pi lg)^2 + (2\pi w + \alpha \sin 2\pi lg)^2}. \end{aligned} \quad (33)$$

Thus the maximum intensity of reflection is displaced by $(\alpha/2\pi) \sin 2\pi lg$ towards the origin of reciprocal space, and the integral breadth in w is $(\alpha/2)(1 - \cos 2\pi lg)$. The displacement is in the direction to be expected, for the mistake increases the average c spacing, and hence decreases the distance of the maximum intensity from the origin of reciprocal space. Both the displacement and the broadening depend on l , and for reflections such that lg is integral they vanish, and become very small if lg is nearly integral. The X-ray reflections will therefore be affected to very different extents, depending on the value of l . Hendricks and Teller (1942) have calculated in detail the $00l$ reflections of a partially dehydrated montmorillonite, which appears to consist of layers of thickness 10 Å and 13 Å with about equal frequency and α about one-half. They give no quantitative comparison with experiment, but state that the qualitative agreement is good. Equation (33) cannot be expected to hold for such a large value of α , but, since Y_m is of the form ρ^m , $H(w)$ can be got by direct summation of equation (24) as a geometric series.

8. The methods of chapter V, paragraph 9, were sufficient for expressing the profiles and integral breadths of lines on powder photographs of imperfect crystals. Nevertheless, expressions in terms of complex quantities are sometimes more convenient for calculation. If $Y(t) = J(t) - iK(t)$ is the mean value of the product FF^* of the structure factors of two cells separated by a distance t in the hkl direction, it is readily found that the line profile is given by

$$I(S) = U^{-1} \int V(t) Y(t) \exp(2\pi i s t) dt, \quad (34)$$

the apparent particle size is, if the maximum is not displaced,

$$\varepsilon = I_s/I = [V Y(0)]^{-1} \int V(t) Y(t) dt, \quad (35)$$

and the integral breadth is given by $\lambda/\varepsilon \cos \theta$. For crystals in which $Y(t)$ decreases rapidly with t , so that the variation of $V(t)$ can be neglected, these reduce to

$$I(S) = (V/U) \int Y(t) \exp(2\pi i s t) dt \quad (36)$$

and

$$\varepsilon = [Y(0)]^{-1} \int Y(t) dt. \quad (37)$$

9. Equation (26) may be used to discuss the distribution of intensity in reciprocal space for single crystals of AuCu_3 containing mistakes. This was of course unnecessary in treating line broadening in Jones and Sykes' powder photographs, but the actual distribution in reciprocal space can be investigated by the scattering from a single crystal (Guinier, 1945; MacGillavry and Strijk, 1946). Sufficient details have not yet been published to show whether or not the distribution of mistakes postulated to explain the powder photographs is correct, but it is of some interest to obtain expressions for the intensity of scattering for the various models.

The values of $Y(x, y, z)$ required follow readily from the values of $J(t)$ for AuCu_3 given on page 83. Since $J(t)$ is the mean value of $AA' + BB'$ for cells separated a distance t in the hkl direction, the real part of $Y(x, y, z)$ will be $J(t)$ with ht/\sqrt{N} replaced by x , kt/\sqrt{N} by y and lt/\sqrt{N} by z . The imaginary part is zero, since $K(t)$ is zero. Thus for the five varieties of mistake $Y(x, y, z)$ has the values

- (i) $(\text{Au} - \text{Cu})^2 \exp \{ -4\alpha\sqrt{(x^2 + y^2 + z^2)}/3a \},$
- (ii) $(\text{Au} - \text{Cu})^2 \exp \{ -4\alpha |x'|/3a \},$
- (iii) $(\text{Au} - \text{Cu})^2 \exp \{ -4\alpha(|x'| + |y'|)/3\sqrt{2}a \},$
- (iv) $(\text{Au} - \text{Cu})^2 \exp \{ -4\alpha(|x| + |y| + |z|)/3\sqrt{3}a \},$
- (v) $(\text{Au} - \text{Cu})^2 \exp \{ -2\alpha(|x''| + |y''|)/a \}.$

In expressions (ii) and (iii) x', y', z' represent x, y, z arranged in the order $|x'| > |y'| > |z'|$, and in expression (v) x'' and y'' are the co-ordinates corresponding to the indices of the same parity. The combination of mistakes of the first and fifth kinds gives

$$\text{(vi)} \quad (\text{Au} - \text{Cu})^2 \exp \{ -[2\alpha'(|x''| + |y''|) + 4\alpha''\sqrt{(x^2 + y^2 + z^2)}/3]/a \},$$

where α' and α'' are the respective probabilities of the two kinds of mistake. For a cubic crystal equation (26) becomes

$$H(u, v, w) = Na^{-3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} Y(x, y, z) \exp \{ -2\pi i(ux + vy + wz)/a \} dx dy dz, \quad (38)$$

and the problem is now only that of performing the integrations with the values of $Y(x, y, z)$ given by expressions (i)–(vi). This is perhaps easiest for (iv) :

$$H(u, v, w)$$

$$= N(\text{Au} - \text{Cu})^2 \left[\int_{-\infty}^{+\infty} \exp \{ -[4\alpha |x| / 3\sqrt{3} + 2\pi i u x] / a \} d(x/a) \right]$$

multiplied by similar integrals in y and z

$$= N(\text{Au} - \text{Cu})^2 \left[\int_0^{\infty} \exp \{ -[4\alpha / 3\sqrt{3} + 2\pi i u](x/a) \} d(x/a) + \text{complex conjugate} \right]$$

multiplied by similar expressions in y and z

$$= N(\text{Au} - \text{Cu})^2 \left[\frac{1}{4\alpha / 3\sqrt{3} + 2\pi i u} + \frac{1}{4\alpha / 3\sqrt{3} - 2\pi i u} \right]$$

multiplied by similar expressions in y and z

$$= N(\text{Au} - \text{Cu})^2 \times \left. \frac{\frac{8\alpha}{3\sqrt{3}}}{\left(\frac{4\alpha}{3\sqrt{3}}\right)^2 + (2\pi u)^2} \cdot \frac{\frac{8\alpha}{3\sqrt{3}}}{\left(\frac{4\alpha}{3\sqrt{3}}\right)^2 + (2\pi v)^2} \cdot \frac{\frac{8\alpha}{3\sqrt{3}}}{\left(\frac{4\alpha}{3\sqrt{3}}\right)^2 + (2\pi w)^2} \right\} \quad (39)$$

The integration for x'' and y'' in (v) is similar, giving

$$H(u, v, w)$$

$$= N(\text{Au} - \text{Cu})^2 \frac{\alpha}{\alpha^2 + (\pi u'')^2} \cdot \frac{\alpha}{\alpha^2 + (\pi v'')^2} \cdot F(w'') \quad (40)$$

where u'' and v'' are the variables in reciprocal space corresponding to the indices of the same parity, and $F(w'')$ is the 'normal' variation of intensity of reflection with the third variable; it is large only for $w'' \sim 0$, and falls to inappreciable values for w'' of the order of the lattice parameter divided by the particle dimensions. This is a

very peculiar distribution of intensity in reciprocal space; the regions of high intensity are disc-like, with the plane of the disc parallel to the directions indicated by the indices of the same parity. Thus for the 100 reflections the disc is perpendicular to the 100 direction, for the 010 reflection to the 010 direction, for the 110 reflection to the 001 direction, for the 211 reflection to the 100 direction, and so forth. The distribution of intensity in reciprocal space is

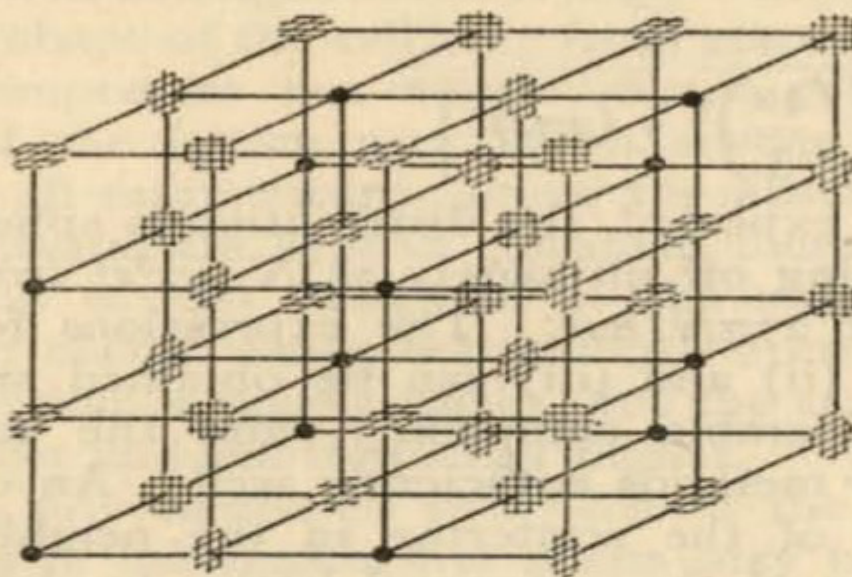


FIG. 2.—Reciprocal lattice for AuCu_3 .

represented diagrammatically in figure 2. The calculation for expression (vi) is more difficult, but it seems that the result would be qualitatively similar to that with (v). The regions of high intensity would be discs with the same orientations, but of appreciable thickness. Unfortunately the single photograph reproduced by Guinier (1945) is insufficient to show if the regions of high intensity are of this form or not. It does show, however, that the sharp reflections are surrounded by a region of diffuse scattering that cannot be explained by mistakes of the type treated here. It is probably an effect of lattice distortion, the copper atoms surrounding a gold atom being displaced somewhat from the lattice points.

The integration for expression (i) is most easily done by transforming to polar co-ordinates with the axis passing

through the point u, v, w . If $s = \sqrt{(u^2 + v^2 + w^2)}$ and $r = \sqrt{(x^2 + y^2 + z^2)}$, equation (38) becomes

$$\begin{aligned}
 H(s) &= N \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp \{ -[4\alpha/3 + 2\pi i s \cos \theta](r/a) \} \\
 &\quad (r/a)^2 \sin \theta d(r/a) d\theta d\phi \\
 &= 2\pi N \int_0^\pi \frac{2 \sin \theta d\theta}{[4\alpha/3 + 2\pi i s \cos \theta]^3} \\
 &= 4\pi N \frac{\frac{8\alpha}{3}}{\left[\left(\frac{4\alpha}{3} \right)^2 + (2\pi s)^2 \right]^{3/2}} \quad (41)
 \end{aligned}$$

As would be expected, the distribution is spherically symmetrical, falling off ultimately as $N/4\pi^3 s^4$ from its initial maximum of $27\pi N/8\alpha^3$. The expressions for H corresponding to (ii) and (iii) can be obtained similarly, but are of considerable complexity, and the simpler cases illustrate the methods sufficiently well. An experimental investigation of the scattering in the neighbourhood of several points of the reciprocal lattice to show definitely if any of the models is correct would be of great interest. A preliminary investigation by Edmunds, Hinde and Lipson (1947) and the work of Strijk and MacGillavry (1946) on reflections of the type $h k \bar{k}$ are in qualitative agreement with model (vi).

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CHAPTER VIII

DISTORTED CRYSTALS

1. IN the crystals discussed so far the lattice has been perfect, or, in other words, the unit cells have been all of the same size and shape, though the contents of the cells may have varied throughout the crystal. Crystals in which the size and shape of the cell vary from place to place form an equally important but more difficult problem. The distortion of the lattice may be of several kinds. For example, at all temperatures above the absolute zero the atoms of a crystal are kept in continual thermal agitation. The agitation is best imagined as the superposition of a number of elastic waves traversing the crystal. These waves are similar to sound waves, but the amplitude is in general smaller and the frequency higher. The frequency is, however, low compared with that of the X-rays, and for purposes of calculation the atoms may be considered at rest, but displaced from their mean positions. This problem is treated in the next chapter. Other sorts of distortion are found in metals used for constructional purposes. Perfect crystals of most metals are soft and easily deformed, and metals in a useful form are generally in a state of internal strain. This may be produced mechanically in drawing or rolling, or 'chemically', by treatment of an alloy in such a way that it begins to separate into two phases, but is not permitted to finish the process. Thus duralumin (about 96 per cent aluminium, 4 per cent copper) in equilibrium at room temperature would consist of a mixture of crystals of practically pure aluminium and of a compound Al_2Cu . As used, however, Cu or Al_2Cu separates in sheets within the aluminium crystals, but on lattices continuous with those of the parent crystals. The unit cells of the aluminium and the new structure will not fit together without a considerable amount of strain, and

the composite crystal is much harder than pure aluminium. In a sense the Cu or Al_2Cu sheets may be regarded as mistakes, but there is a variation of lattice parameter as well as of cell contents. Another example of a variation of lattice parameter within the individual crystals is given by alloys with compositions in the neighbourhood of Cu_4FeNi_3 . The alloys are in themselves of no particular importance, but it happens that the lattice parameter is approximately a sinusoidal function of position within the crystal, so that the theoretical treatment is comparatively straightforward and the interpretation of the photographs easy.

2. The alloy Cu_4FeNi_3 has been investigated by Daniel and Lipson (1943, 1944). In equilibrium above about 800°C . it consists of cubic crystals of one kind only, but below this temperature it consists of a mixture of cubic crystals of two kinds, differing in composition. If a specimen in equilibrium above 800°C . is held at a lower temperature (say 650°C .) for a time insufficient to reach equilibrium, a state intermediate between that of perfect crystals of one kind and that of perfect crystals of two kinds is obtained, and can be maintained indefinitely by cooling the specimen to room temperature. In the intermediate state the lines on powder photographs are sharp, but are flanked by satellite lines, whose existence can be explained by the presence in the crystals of layers perpendicular to the crystal axes and alternately copper-rich and copper-poor. These will have a varying lattice parameter in the direction perpendicular to the layers, and the assumption that the variation is sinusoidal accounts for most of the details of the photographs. Since Fe, Ni and Cu have approximately the same atomic number the structure amplitudes of the cells will vary little, and may be taken as independent of position.

Consider, therefore, a crystal approximately cubic, but with the lattice parameter varying sinusoidally in the x direction from $a - \delta$ to $a + \delta$, the wave-length of the

variation being L . Then the position of the n^{th} unit cell will be given by

$$\left. \begin{aligned} x_n &= n_1 a + (L\delta/2\pi a) \cos (2\pi n_1 a/L), \\ y_n &= n_2 a, \\ z_n &= n_3 a, \end{aligned} \right\} \quad (1)$$

since the distance in the x direction between the origins of successive cells is

$$\begin{aligned} & [(n_1 + 1)a + (L\delta/2\pi a) \cos \{2\pi(n_1 + 1)a/L\}] \\ & \quad - [n_1 a + (L\delta/2\pi a) \cos (2\pi n_1 a/L)] \\ &= a + (L\delta/2\pi a) [\cos (2\pi n_1 a/L) \cos (2\pi a/L) \\ & \quad - \sin (2\pi n_1 a/L) \sin (2\pi a/L) - \cos (2\pi n_1 a/L)] \end{aligned}$$

which becomes

$$a - \delta \sin (2\pi n_1 a/L), \quad (2)$$

since a is small compared with L , and $\cos (2\pi a/L) \doteq 1$, $\sin (2\pi a/L) \doteq 2\pi a/L$. If h', k', l' (not necessarily integral) are co-ordinates in reciprocal space, the amplitude of reflection as a function of position in reciprocal space will be given by

$$\begin{aligned} G(h', k', l') &= F \sum_n \exp \{2\pi i [h' x_n + k' y_n + l' z_n]/a\} \\ &= F \sum_n \exp \{2\pi i [n_1 h' + (L\delta h'/2\pi a^2) \cos (2\pi n_1 a/L) \\ & \quad + n_2 k' + n_3 l']\} \quad (3) \end{aligned}$$

where F is the structure amplitude of one unit cell. As a function of k' and l' this is normal, and has large values only for $k' \doteq k$, $l' \doteq l$, where k and l are integral. Its behaviour as a function of h' , however, requires special investigation. Let us consider therefore

$$\begin{aligned} G(h') &= F \sum_n \exp \{2\pi i [nh' + (L\delta h'/2\pi a^2) \cos (2\pi na/L)]\} \\ &= F \sum_n \exp \{2\pi i nh'\} \cdot \exp \{2\pi i (L\delta h'/2\pi a^2) \cos (2\pi na/L)\} \quad (4) \end{aligned}$$

If δ is so small that $L\delta h'/a^2$ is small compared with unity, the second exponential in equation (4) may be replaced by

the first two terms of its power series :

$$\begin{aligned} \exp \{2\pi i(L\delta h'/2\pi a^2) \cos (2\pi na/L)\} \\ \doteq 1 + i(L\delta h'/a^2) \cos (2\pi na/L) \\ = 1 + i(L\delta h'/2a^2) \exp \{2\pi ina/L\} \\ + i(L\delta h'/2a^2) \exp \{-2\pi ina/L\}, \end{aligned} \quad (5)$$

and equation (4) becomes

$$\begin{aligned} G(h') = F \sum_n \exp \{2\pi i n h'\} \\ + iF(L\delta h'/2a^2) \sum_n \exp \{2\pi i n (h' + a/L)\} \\ + iF(L\delta h'/2a^2) \sum_n \exp \{2\pi i n (h' - a/L)\}. \end{aligned} \quad (6)$$

The first of these sums has a maximum of amplitude proportional to F at $h' = h$, where h is any integer ; the second has a maximum of amplitude proportional to $F(L\delta h'/2a^2)$ at $h' + a/L = h$, where h is any integer ; and the third has a similar maximum at $h' - a/L = h$, where h is any integer. Thus, in addition to a strong reflection at the points of the reciprocal lattice, there are weaker ones at distances of $\pm a/L$ from it. The intensities are in the ratio

$$[L\delta(h - a/L)/2a^2]^2 : 1 : [L\delta(h + a/L)/2a^2]^2,$$

or approximately $(L\delta h/2a^2)^2 : 1 : (L\delta h/2a^2)^2$. The intensities of the extra maxima, or 'side-bands' as they have been called, increase as the square of the order of reflection.

3. For comparison with this result it is interesting to work out the reflection from a structure in which the structure amplitude, instead of the lattice parameter, varies sinusoidally.

$$\text{If } \left. \begin{aligned} x_n &= na, \\ F_n &= F[1 + g \cos (2\pi na/L)], \end{aligned} \right\} \quad (7)$$

where g is a fraction and L is the wave-length of the variation, the amplitude of reflection is

$$\begin{aligned} G(h') &= F \sum_n [1 + g \cos (2\pi na/L)] \exp \{2\pi i n h'\} \\ &= F \sum_n \exp \{2\pi i n h'\} + F(g/2) \sum_n \exp \{2\pi i n (h' + a/L)\} \\ &\quad + F(g/2) \sum_n \exp \{2\pi i n (h' - a/L)\}. \end{aligned} \quad (8)$$

As before, the three sums lead to maxima at $h' = h$,

$h \pm a/L$, where h is any integer, but the intensities are in the ratio $g^2/4 : 1 : g^2/4$, so that the side-bands are the same in all orders. In particular, there are side-bands flanking the origin of the reciprocal lattice ($h = 0$), whereas these are of vanishingly small intensity for lattice parameter variation. Bragg and Lipson (1943) have devised gratings that illustrate the different diffraction phenomena caused by mistakes, variation of structure amplitude, and variation of lattice parameter.

4. Sinusoidal variation of lattice parameter in the x direction gives subsidiary reflections at $h \pm a/L$. In a cubic crystal there is nothing to distinguish the x direction from the y and z directions, and one would expect variations in these directions also, either coexisting through the crystal, or taking place in separate regions. The investigations of Daniel and Lipson (1944) indicate that the latter is more likely. Points of the reciprocal lattice of the form h, k, l will thus be accompanied by three pairs of subsidiary reflections, the intensities being proportional to h^2, k^2, l^2 . Those of the form $h, k, 0$ will have only two pairs, since one of the indices is zero, and those of the form $h, 0, 0$ will have only one pair. The separation of the subsidiary reflections from the main line in a powder photograph will not be a simple function of θ , but will depend on the indices of the reflection. This may be seen as follows. (Compare chapter VI, paragraph 2.) A reflection whose indices are h, k, l will reflect at an angle θ given by

$$(2a/\lambda)^2 \sin^2 \theta = h^2 + k^2 + l^2.$$

One whose indices are $h + a/L, k, l$ will reflect at the slightly greater angle $\theta + \delta\theta$ given by

$$(2a/\lambda)^2 \sin^2 (\theta + \delta\theta) = (h + a/L)^2 + k^2 + l^2,$$

or approximately

$$(2a/\lambda)^2 \sin \theta \cos \theta \delta\theta = ha/L,$$

$$\delta\theta = \frac{h}{\sqrt{(h^2 + k^2 + l^2)}} \cdot \frac{\lambda}{2L} \cdot \sec \theta. \quad (9)$$

The separation of the side-bands is thus greatest for reflections of the form $h00$, and least for those of the form hhh . If h , k and l are all non-zero and unequal there will be three side-bands on each side of the main line, and their overlapping with the main line and one another makes measurements of intensities difficult.

5. Equation (8) for the amplitude of reflection from a structure with sinusoidal variation of structure amplitude does not involve any approximations, but equation (6) for variation of lattice parameter depends on the assumption that $L\delta h'/a^2$ is small compared with unity. An exact treatment hardly comes within the scope of this book, but it may be remarked that the second exponential in equation (4) is represented exactly by the series

$$\begin{aligned} \exp \{i(L\delta h'/a^2) \cos (2\pi na/L)\} = & J_0(L\delta h'/a^2) \\ & + 2iJ_1(L\delta h'/a^2) \cos (2\pi na/L) \\ & - 2J_2(L\delta h'/a^2) \cos (2\pi n \cdot 2a/L) \\ & - 2iJ_3(L\delta h'/a^2) \cos (2\pi n \cdot 3a/L) + \dots, \end{aligned} \quad (10)$$

where J_0, J_1, J_2, \dots are Bessel functions of the 0th, 1st, 2nd, ... order. Each reciprocal lattice point is therefore flanked by a series of side-bands at distances of $\pm a/L$, $\pm 2a/L$, $\pm 3a/L$, ..., the intensities of the central reflection being proportional to J_0^2 , and the intensities of the others being proportional to J_1^2, J_2^2, \dots . It is a property of Bessel functions that

$$J_0^2 + 2J_1^2 + 2J_2^2 + \dots = 1, \quad (11)$$

so that the total intensity is the same as that from an undistorted lattice. (There is only one central maximum, but two side-bands of intensity J_1^2 , two of J_2^2 , &c.) Daniel and Lipson (1944) find that the higher order side-bands do appear, and that when all factors are taken into account the intensities are in agreement with expectation. One of the difficulties is 'extinction', a phenomenon that reduces the intensities of the main lines relative to those of the side-bands. The original paper must be consulted for full details.

6. X-ray diffraction from aluminium crystals containing 4 per cent by weight (1.75 per cent by atoms) of copper has been investigated by Preston (1938) and Guinier (1938). The phenomenon is somewhat complicated; at room temperature layers of copper segregate on planes perpendicular to the axes of the parent crystal, but at higher temperatures (about 200° C.) the copper layers 'evaporate' and layers of Al_2Cu form. The Al_2Cu has not its usual structure, but one similar to that of fluorite (CaF_2), apparently because this structure can fit into the aluminium lattice with less strain. The sheets of Cu atoms at room temperature appear to be about 45 Å square, 200 Å apart, and about two atomic layers thick. The layers of Al_2Cu produced at higher temperatures are considerably larger, and their diffraction effects sharper. No detailed treatment of the diffraction effects has been given in either case, but there is one very interesting phenomenon. The X-ray photographs show streamers from the ordinary reflections on one side only, in a way that indicates that the intensity of reflection in reciprocal space is not symmetrical about the points of the reciprocal lattice. The $h k l$ reflection has streaks running out towards $h + 1, k, l$; $h, k + 1, l$; and $h, k, l + 1$; but not towards $h - 1, k, l$; $h, k - 1, l$; or $h, k, l - 1$. This is one of the few phenomena that are not effectively symmetrical about the points of the reciprocal lattice, and is at first sight rather puzzling. It is, however, qualitatively explained by a combination of varying lattice parameter and varying structure amplitude. Copper atoms are smaller than aluminium atoms, and contain more electrons, so that the scattering factor is high where the spacing is low, and vice versa. If both vary sinusoidally

$$\left. \begin{aligned} x_n &= na + (L\delta/2\pi a) \cos(2\pi na/L), \\ \text{and } F_n &= F[1 + g \sin(2\pi na/L)] \end{aligned} \right\} \quad (12)$$

in order to 'synchronize' the variations in the way postulated above the wave-length L must be the same in both

x_n and F_n , and one must vary as the cosine, the other as the sine. The amplitude of reflection as a function of h' is then

$$G(h') = \sum_n F_n \exp \{2\pi i h' x_n / a\} \quad (13)$$

$$= F \sum_n [1 + g \sin (2\pi n a / L)] \exp \{2\pi i h' [n + (L\delta / 2\pi a^2) \cos (2\pi n a / L)]\},$$

which becomes, on expanding and neglecting products of small terms,

$$\begin{aligned} G(h') = & F \sum_n \exp \{2\pi i n h'\} \\ & + iF[(L\delta h' / 2a^2) - g/2] \sum_n \exp \{2\pi i n (h' + a/L)\} \\ & + iF[(L\delta h' / 2a^2) + g/2] \sum_n \exp \{2\pi i n (h' - a/L)\}. \end{aligned} \quad (14)$$

The first of these sums gives a maximum of intensity proportional to F^2 at $h' = h$, where h is any integer, the second gives a maximum of intensity proportional to $F^2(L\delta h' / 2a^2 - g/2)^2$ for $h' = h - a/L$, and the third a maximum of intensity proportional to $F^2(L\delta h' / 2a^2 + g/2)^2$ for $h' = h + a/L$. It is clear that the inner maximum will be weaker than the outer, and will practically vanish if $L\delta h/a^2$ is approximately equal to g . This simple model gives merely a pair of extra spots accompanying the main reflection, but it is not to be expected that L will be constant throughout the crystal, and a proper treatment would undoubtedly give a continuous streak extending from the main reflection towards $h + 1$, the intensity on the high-order side being greater than on the low-order side. Similar layers perpendicular to the y and z axes will produce streaks running outwards towards $k + 1$ and $l + 1$.

7. After suitable heat treatment ('annealing') the spots or lines on X-ray photographs of metals are sharp, but if the metal is deformed by bending, twisting, rolling, drawing, hammering, &c., the spots spread out into Debye-Scherrer lines, and the lines become broadened. Clearly the original perfection of the crystal lattice has been lost, but there has been some controversy over the nature of the

imperfection. There have been three main suggestions :

- (i) that the metal is broken up into ' crystallites ' so small (10^{-5} to 10^{-6} cm. in linear dimensions) that diffraction broadening occurs ;
- (ii) that the metal is broken up into crystals (about 10^{-4} cm. in linear dimensions) with differing lattice parameters ; and
- (iii) that the crystals of the metal remain fairly large (about 10^{-4} cm. in linear dimensions), but are elastically distorted.

The distinction between the second and third suggestions lies chiefly in the nature of the distortion. According to the second the distortion is merely a uniform expansion or contraction of the whole crystal, whereas the third includes non-uniform expansion or contraction, as well as twists and bends.

A careful study of the variation of the line-broadening with wave-length, Bragg angle, and indices of reflection can decide between the suggestions. The first would yield a broadening increasing with $\lambda \sec \theta$, and possibly varying somewhat with the indices of reflection, if the crystallites tended to have a more or less regular non-spherical shape. The second would yield a broadening increasing with $\tan \theta$, but independent of λ and the indices of reflection. The third would yield a broadening increasing with $\tan \theta$ and independent of λ , but it would be independent of the indices of reflection only if the tensile strain were, on the average, independent of crystallographic direction. Most crystals (tungsten seems to be an exception) are not elastically isotropic, so that strain independent of direction would imply a variation of stress with direction. On general considerations of static equilibrium it seems likely that stress, rather than strain, would tend on the average to be independent of direction, with a consequent variation of the strain, and a dependence of the line-broadening on the indices of reflection.

On these qualitative considerations the experimental evidence is unquestionably in favour of the third suggestion. It is found that the broadening increases with $\tan \theta$ and not with $\sec \theta$ (Brindley, 1940; Stokes, Pascoe and Lipson, 1943; Smith and Stickley, 1943), is independent of the wave-length of the X-rays (the same references, and Lipson and Stokes, 1943), and depends markedly on crystallographic direction (Wood, 1932; Stokes, Pascoe and Lipson; Smith and Stickley). Though the experimental evidence makes it almost certain that lattice distortion is the main cause of the line-broadening, the theoretical problem of relating quantitatively the breadth of the lines and the properties of the crystal remains. It is as much a problem in the theory of elasticity as in X-ray diffraction, and possibly the nature of the glide processes by which excessive strains in the lattice are relieved must be taken into account also. No exact solution has been found, and perhaps each type of metal and each mode of deformation requires special treatment. It is, however, possible to give an approximate general theory.

8. For calculating the line-broadening it is necessary to know $Y(t)$, the mean value of FF^* for two cells separated a distance t in the $h k l$ direction (chapter VII, paragraph 8). In a distorted crystal the structure amplitude of a cell at (x, y, z) will differ from that at $(0, 0, 0)$ for two reasons: the cell is displaced bodily, and it suffers a rotation. It is hardly possible to evaluate $Y(t)$ without assuming a particular variety of distortion. It will, however, be true in general that for large values of t the relative displacement of the cells will be large and random, and $Y(t)$ will therefore vanish. For t small the displacement of one cell relative to another a distance t away will be e_h , the local value of the strain in the $h k l$ direction, multiplied by t . The effect of the rotation on the phase of the scattered X-rays is small compared with that of the displacement, and may be neglected in a first approximation. The structure amplitudes of the two cells will

therefore differ only through a phase factor

$$\exp \{2\pi i S e_h t\}, \quad . \quad . \quad . \quad (15)$$

where $S \equiv 2 \sin \theta / \lambda$ is the distance from the reciprocal lattice point in question to the origin.* The required function $Y(t)$ is then the mean value of

$$FF^* = F^2 \exp \{2\pi i S e_h t\}. \quad . \quad . \quad (16)$$

If the fraction of the crystal for which e_h lies between e and $e + de$ is $\psi_h(e) de$, this mean value becomes

$$Y(t) = F^2 \int_{-\infty}^{+\infty} \psi_h(e) \exp \{2\pi i S e t\} de, \quad . \quad (17)$$

and the apparent particle size is

$$\begin{aligned} \varepsilon &= [Y(0)]^{-1} \int_{-\infty}^{+\infty} Y(t) dt \\ &= \int_{-\infty}^{+\infty} \left[\int_{-\infty}^{+\infty} \psi_h(e) \exp \{2\pi i S e t\} de \right] dt \\ &= S^{-1} \int_{-\infty}^{+\infty} \left[\int_{-\infty}^{+\infty} \psi_h(e) \exp \{2\pi i (St)e\} de \right] d(St), \\ &= S^{-1} \psi_h(0), \quad . \quad . \quad . \quad . \quad . \quad (18) \end{aligned}$$

by the relations between Fourier transforms (chapter VII, paragraph 5). The integral breadth of the reflection is

$$\beta = \lambda / \varepsilon \cos \theta = 2 \tan \theta / \psi_h(0). \quad . \quad . \quad (19)$$

For a given reflection β increases with $\tan \theta$ and is independent of λ , as stated above, and

$$\psi_h(0) = 2 \tan \theta / \beta. \quad . \quad . \quad . \quad (20)$$

Measurement of integral breadths thus gives the fraction

* In a cubic crystal the components of the relative displacement along the crystal axes are $e_h t \cdot h / \sqrt{N}$, $e_h t \cdot k / \sqrt{N}$, $e_h t \cdot l / \sqrt{N}$, where $N = h^2 + k^2 + l^2$. The difference in phase between the rays scattered by the two cells is therefore

$$2\pi(h \cdot e_h t h / \sqrt{N} + k \cdot e_h t k / \sqrt{N} + l \cdot e_h t l / \sqrt{N}) / a$$

$$= 2\pi \sqrt{N} e_h t / a = 2\pi (2 \sin \theta / \lambda) e_h t.$$

The expression is, however, valid for non-cubic crystals (Stokes and Wilson, 1944).

of the crystal for which there is no strain in the hkl direction. In fact, it is fairly easy to show that when proper allowance is made for other causes of line-broadening the line profile is $\psi_h(-e \cot \theta)$ within a proportionality factor. The negative sign merely indicates that places where the lattice is expanded reflect at lower angles than the ideal, and places where the lattice is contracted at higher angles.

Equation (20) may be regarded as a complete, though approximate, solution of the diffraction problem. There remains the problem of evaluating $\psi_h(0)$ in terms of the elastic, and perhaps the plastic, properties of the substance. One simple assumption is that $\psi_h(0)$ is inversely proportional to the maximum strain in the hkl direction, and that this is given by the maximum stress, assumed independent of direction, divided by the value of Young's modulus for the hkl direction. For a cubic substance this gives

$$\beta \cot \theta = A + BH$$

$$\left. \begin{aligned} \text{where } A &= 4p_{\max.} s_{11}, \\ B &= -8p_{\max.} (s_{11} - s_{12} - 2s_{44}), \\ H &= (h^2 k^2 + k^2 l^2 + l^2 h^2) / (h^2 + k^2 + l^2)^2; \end{aligned} \right\} \quad (21)$$

$p_{\max.}$ is the maximum stress and s_{11} , s_{12} , s_{44} are elastic constants. Stokes, Pascoe and Lipson (1943) have found that this equation gives quite good agreement with experiment, and that $p_{\max.}$ is approximately the same as the known values of the yield stress (Megaw *et al.*, 1944, 1945), but Smith and Stickley found only qualitative agreement. Stokes and Wilson (1944) have attempted to take shear stresses as well as direct stresses into account, using the approximation of paragraph 4, chapter VII, for the mean value of FF^* . This gives

$$Y(t) = \langle F^2 \exp \{2\pi i S e_h t\} \rangle = F^2 \exp \{-2\pi^2 S^2 t^2 \langle e_h^2 \rangle\}$$

$$\text{and } \varepsilon = [Y(0)]^{-1} \int_{-\infty}^{+\infty} Y(t) dt = S^{-1} (2\pi \langle e_h^2 \rangle)^{-\frac{1}{2}},$$

$$\beta \cot \theta = 2\sqrt{(2\pi \langle e_h^2 \rangle)}.$$

Thus $\beta \cot \theta$ is proportional to the root mean square value of the strain in the hkl direction. On the assumption that the stress is on the average spherically symmetrical this leads to

$$\beta \cot \theta = \sqrt{(A + BH)}$$

$$\left. \begin{aligned} \text{where } A &= 8\pi \{ (s_{11} + 2s_{12}^2) \langle p_{11}^2 \rangle - 4s_{12}(s_{12} + 2s_{11}) \langle p_{12}^2 \rangle \} \\ B &= -32\pi \{ (s_{11} - s_{12})^2 - 4s_{44}^2 \} \langle p_{12}^2 \rangle ; \end{aligned} \right\} \quad (22)$$

$\langle p_{11}^2 \rangle$ and $\langle p_{12}^2 \rangle$ are the mean square values of the direct and shear stresses and H has the same value as before. The experimental results so far do not appear to be sufficiently accurate to decide whether (21) or (22) is the better approximation.

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CHAPTER IX

EFFECTS OF THERMAL MOTION

1. THE atoms forming a crystal are in a state of continual agitation about their mean positions. The period of vibration of an atom is very small compared with the time required for taking an X-ray photograph, so that the photograph records the time average of the X-ray scattering. The period of vibration of an atom is, on the other hand, large compared with the period of vibration of X-rays, so that at any instant the scattering is the same as if the atoms were at rest, but displaced from their mean positions. For the interpretation of X-ray photographs it is therefore necessary to find the time average of the scattering from a crystal in which the atomic displacements take on all values appropriate to its temperature. The calculation falls naturally into two stages: (i) the determination of what functions of the atomic displacements are involved in the average scattering, and (ii) the determination of the average values of these functions in terms of the absolute temperature and the elastic constants of the crystal.

2. Suppose that because of the thermal agitation the origin of the n^{th} unit cell is displaced from its mean position of $x_n = n_1a$, $y_n = n_2b$, $z_n = n_3c$, to

$$\left. \begin{aligned} x'_n &= n_1a + X_n, \\ y'_n &= n_2b + Y_n, \\ z'_n &= n_3c + Z_n. \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

The effective structure factor of the cell will therefore be changed from F to

$$F_n = F \exp \{2\pi i(hX_n/a + kY_n/b + lZ_n/c)\}. \quad (2)$$

It is here assumed that the unit cell is displaced as a whole, which is not strictly true for crystals with more than one atom per unit cell, but it will be seen later that the assump-

tion is justifiable. The function determining the scattering from any imperfect crystal is Y_m , the mean value over position in the crystal of $F_n F_{n+m}^*$ for two cells separated by the translation $m_1 a$, $m_2 b$, $m_3 c$ (chapter VII, equation (24)). Thus the problem is to find the mean value of

$$F_n F_{n+m} = F^2 \exp \{2\pi i [h(X_n - X_{n+m})/a + k(Y_n - Y_{n+m})/b + l(Z_n - Z_{n+m})/c]\}. \quad (3)$$

The average value of this over all cells in a crystal at any instant is equal to its time average for a given pair of cells with the required separation. It was shown in chapter VII that the mean value of $\exp(ix)$ is approximately $\exp(-\frac{1}{2}\langle x^2 \rangle)$, so that, if quantities belonging to the first cell are unprimed, and those belonging to the second cell are primed, the average value of equation (3) is

$$Y_m = F^2 \exp \{-2\pi^2 \langle [h(X - X')/a + k(Y - Y')/b + l(Z - Z')/c]^2 \rangle\}, \quad (4)$$

where the angle brackets represent a time average. As a matter of fact the result of using this approximation is here correct, though the proof of its correctness is difficult (Born, 1942-3). The expression to be averaged is easily rearranged to

$$\left. \begin{aligned} & (hX/a + kY/b + lZ/c)^2 + (hX'/a + kY'/b + lZ'/c)^2 \\ & - 2(hX/a + kY/b + lZ/c)(hX'/a + kY'/b + lZ'/c). \end{aligned} \right\} \quad (5)$$

The first two terms are always positive, being perfect squares, and will have the same mean value. Let

$$M = 2\pi^2 \langle (hX/a + kY/b + lZ/c)^2 \rangle, \quad (6)$$

where M is necessarily positive. At first one might think that the average value of the third term would be zero, except for the special case $m_1 = m_2 = m_3 = 0$, when it would cancel the first two. Cells close together in the crystal, however, will on the whole tend to move in the same way, the tendency diminishing with increasing separation of the cells. The average value of the third term will not vanish, therefore, but will start at $-2M$ for the m 's all zero, and

decrease numerically to zero with increase in the m 's. Let

$$P_m = 4\pi^2 \langle (hX/a + kY/b + lZ/c) (hX'/a + kY'/b + lZ'/c) \rangle. \quad (7)$$

Since this is symmetrical in the primed and unprimed letters $P_m = P_{-m}$. Equation (4) becomes

$$Y_m = F^2 \exp (P_m - 2M). \quad (8)$$

Since P_m decreases from $2M$ to 0 as m increases, Y_m decreases from its initial value of F^2 , approaching the constant value $F^2 \exp (-2M)$ asymptotically. We have seen that a constant value of Y_m means a sharp reflection, and a value decreasing to zero means a broadened reflection. In the present case Y_m can be regarded as the sum of two parts; a constant part $F^2 \exp (-2M)$, and a variable part, which it is convenient to write $F^2 W_m$, decreasing from an initial value of $F^2 [1 - \exp (-2M)]$ to zero with increasing m . Equation (8) becomes

$$\left. \begin{aligned} Y_m &= F^2 \exp (-2M) + F^2 W_m, \\ \text{where } W_m &= [\exp (P_m) - 1] \exp (-2M), \end{aligned} \right\} \quad (9)$$

and the average intensity of reflection from the crystal as a function of position in reciprocal space is (chapter VII, equation (24))

$$H(u, v, w) = H_1(u, v, w) + H_2(u, v, w) \quad (10)$$

where

$$\left. \begin{aligned} H_1(u, v, w) &= U^{-1} F^2 \exp (-2M) \sum_m V_m \\ &\quad \exp \{ -2\pi i (m_1 u + m_2 v + m_3 w) \} \\ \text{and} \\ H_2(u, v, w) &= U^{-1} F^2 \sum_m V_m W_m \\ &\quad \exp \{ -2\pi i (m_1 u + m_2 v + m_3 w) \}. \end{aligned} \right\} \quad (11)$$

The first of these is the ordinary expression for the intensity of reflection from a perfect crystal, except that it is diminished by the factor $\exp (-2M)$. The second is like that for the intensity of reflection from a crystal containing mistakes. The scattering from a crystal in thermal agitation consists therefore of two parts, the first the same,

except for a reduction in intensity, as that from a perfect crystal with stationary atoms, and the second a broad reflection similar to that from a crystal with mistakes. Since W_m is equal to W_{-m} the maximum of the broadened reflection will coincide in reciprocal space with that of the sharp. The total intensity, the integral of the sum of the two parts over one cell of the reciprocal lattice, is the same as that from an undisturbed crystal. In general W_m decreases very rapidly with m , and the broadened part of the reflection may be written

$$H_2(u, v, w) = (V/Uabc)F^2 \iiint W(x, y, z) \exp \{-2\pi i(xu/a + yv/b + zw/c)\} dx dy dz \quad (12)$$

where $x = m_1a$, $y = m_2b$, $z = m_3c$ and the integrations extend from $-\infty$ to $+\infty$. Within a factor, therefore, H_2 is the Fourier transform of W .

3. Logically the next step is to evaluate M and P_m in terms of the absolute temperature and elastic constants of the crystal, but a digression on their physical significance and qualitative behaviour is perhaps desirable. The interpretation of M is the simpler, being $2\pi^2 S^2$ times the mean square displacement of the cells in the hkl direction. This is easily seen for a cubic crystal, for then

$$\begin{aligned} M &= 2\pi^2 \langle (hX/a + kY/b + lZ/c)^2 \rangle \\ &= 2\pi^2 \frac{h^2 + k^2 + l^2}{a^2} \langle (h'X + k'Y + l'Z)^2 \rangle \\ &= 2\pi^2 S^2 \langle (h'X + k'Y + l'Z)^2 \rangle, \end{aligned} \quad (13)$$

where h' , k' , l' , the indices of reflection divided by

$$\sqrt{(h^2 + k^2 + l^2)},$$

are the direction cosines of the hkl direction. The expression in parentheses is the component of the displacement X , Y , Z in the direction determined by h' , k' , l' , or, in other words, the displacement in the hkl direction. For crystals of other systems the geometry is more complicated, but the result is the same.

Since the intensity of the sharp component of the reflection is reduced by the factor $\exp(-2M)$, temperature motion reduces the intensity of all sharp reflections. The reduction is on the whole greater for the higher orders, that is, those with large values of $S = 2 \sin \theta / \lambda$, but it is a smooth function of S only if the crystal is cubic or elastically isotropic. The mean-square displacement will be greatest in directions in which the restoring forces acting on the atoms are least, and the intensity of reflection from planes perpendicular to these directions will be lower than that from other planes. The effect is very marked in substances like graphite, in which displacements perpendicular to the layers are much easier than displacements in the layers.

In a similar way it can be shown that P_m is $4\pi^2 S^2$ times the mean value of the product of the displacements in the hkl direction of two cells separated by the translation $m_1 a$, $m_2 b$, $m_3 c$. This will depend not only on the ease of displacement in the hkl direction, but also on the relation between this direction and the translation relating the cells. Thus P_m and M will be large for the same points of the reciprocal lattice, but for a given point P_m will be largest when the translation $m_1 a$, $m_2 b$, $m_3 c$ lies in directions for which the crystal is not easily deformable, since the correlation between the motions of the cells will be greatest for these directions, and it will be least when the translation lies in directions for which the crystal is easily deformable. The same is true for W_m ; it will be large for the translation lying along relatively undeformable directions, and small for it lying along readily deformable directions. The intensity of the fuzzy part of the reflection is related to W_m by equation (12), whence it follows that the variation of $H_2(u, v, w)$ with u, v, w is the converse of that of W_m with m_1, m_2, m_3 . Thus there will be streaks of comparatively strong intensity in directions for which the crystal is easily deformed, and regions where the scattered intensity is weak corresponding to directions for which the crystal is not easily deformed. This behaviour

is similar to that of the scattering from small crystals, discussed in chapter III. The region of scattering is extended in directions for which the dimension of the crystal is least (face perpendiculars), and is contracted in directions for which the dimension of the crystal is greatest (corners). Small thickness corresponds to easy deformability and large thickness to difficult.

4. The evaluation of M and W_m bears many resemblances to the calculation of the heat capacity of crystals. The motion of the atoms can be analysed in terms of 'normal co-ordinates', each of which is equivalent to a wave of definite frequency traversing the crystal. There are three times as many normal co-ordinates as there are atoms in the crystal, the number of 'degrees of freedom' being the same whether the motion is regarded as made up of waves, or of motions of individual atoms. If there are more than one atom in the true unit cell, the waves divide into two groups, called 'acoustic' and 'optical'. The former are of low frequency, with wave-lengths large compared with the cell dimensions, and the latter are of high frequency, with wave-lengths less than the cell dimensions. The number of waves in the acoustic group is $3N$, where N is the number of unit cells, the remaining waves being optical. The energy of the crystal is equal to the sum of the energies possessed by the waves. It is known from quantum theory that the average energy of a vibration of frequency ν at the absolute temperature T is

$$E_\nu = \frac{h\nu}{\exp(h\nu/kT) - 1} + \frac{1}{2}h\nu \left\{ \begin{array}{l} \\ \approx kT \text{ for } T \gg h\nu/k. \end{array} \right. \quad (14)$$

In this equation h is Planck's constant and k is Boltzmann's constant. If the number of waves per unit volume with frequencies between ν and $\nu + d\nu$ is $Q_\nu d\nu$, the total energy of a crystal of volume V is

$$E = V \int E_\nu Q_\nu d\nu, \quad (15)$$

the range of integration covering all frequencies. The heat capacity per unit volume is then $C_v = V^{-1}(\partial E/\partial T)_v$. The well-known Debye expressions for E and C_v follow from the assumption that the crystal behaves as an elastically isotropic continuum for frequencies up to a certain maximum ν_m , fixed by the requirement that the total number of frequencies should be three times the number of atoms. It is clear that this assumption applied to the problem of thermal scattering will obscure most of the interesting effects, since the mean-square displacement will be independent of direction, so that the weakening of the sharp maximum will depend only on S^2 and not on h, k, l , and the cloud of diffuse scattering around the sharp maximum will be spherically symmetrical and show no streamers or other peculiar effects. A detailed treatment of M and W_m would, however, require an extensive knowledge of lattice dynamics, and we must confine ourselves to the Debye evaluation of M and a first approximation to the diffuse scattering. In order to keep the equations as simple as possible we shall assume that the axes are orthogonal and that there is one atom per unit cell.

5. A single wave of frequency ν traversing the crystal will displace the n^{th} unit cell in the hkl direction by an amount varying sinusoidally with the time. Actually there are always three independent waves of a given wave-length—corresponding to the one longitudinal and the two transverse waves in an isotropic medium—and in the evaluation of M we may assume that one of these is responsible for the displacement in the hkl direction, and the other two are responsible for the displacements at right angles to it. The displacement of the n^{th} unit cell in the hkl direction is then of the form

$$\xi_\nu = A_\nu \cos 2\pi\nu t, \quad . \quad . \quad . \quad (16)$$

where A_ν is the amplitude of the wave of frequency ν . To calculate M we want the mean value of ξ^2 as a function of the absolute temperature, and this is obtainable by

way of the energy of the vibrating crystal. Since the mean value of \cos^2 is one-half, $\langle \xi_v^2 \rangle = \frac{1}{2} \langle A_v^2 \rangle$. The kinetic energy of the cell is $\frac{1}{2} \mu \dot{\xi}_v^2 = 2\pi^2 \nu^2 \mu A_v^2 \sin^2 2\pi \nu t$, where μ is the mass of the cell, so that the mean value of the kinetic energy is $\pi^2 \nu^2 \mu \langle A_v^2 \rangle$. The mean energy of the cell is twice this, the mean values of the potential and the kinetic energies being equal, so that the total energy of the crystal due to this wave is

$$E_v = 2N\pi^2 \nu^2 \mu \langle A_v^2 \rangle,$$

so that $\langle \xi_v^2 \rangle = \frac{1}{2} \langle A_v^2 \rangle = E_v / 4\pi^2 N \mu \nu^2$. . . (17)

The mean-square displacement of a cell in the hkl direction is given by equation (17) summed for all values of ν that are effective, so that

$$\begin{aligned} M &= 2\pi^2 S^2 \langle \xi^2 \rangle \\ &= 2\pi^2 S^2 \cdot \frac{1}{3} \int \langle \xi^2 \rangle V Q_\nu d\nu \\ &= \frac{S^2 V}{6N\mu} \int \frac{E_\nu Q_\nu}{\nu^2} d\nu. \end{aligned} \quad . \quad . \quad . \quad (18)$$

The factor of one-third comes in because only one-third of the waves are effective in producing displacements in the hkl direction. For an isotropic medium, as assumed in the Debye theory, $Q_\nu = 12\pi C^{-3} \nu^2$, where C is an average value of the speed of propagation of elastic waves. The derivation of this equation will be found in any good textbook on heat, for example, in chapter XX of *Heat and Thermodynamics* by J. K. Roberts. Thus on the assumptions of the Debye theory

$$M = \frac{2\pi S^2 V}{N\mu C^3} \int_0^{\nu_m} E_\nu d\nu = \frac{2\pi S^2}{\rho C^3} \int_0^{\nu_m} E_\nu d\nu, \quad . \quad (19)$$

where ρ is the density of the crystal. Since

$$\begin{aligned} 12\pi C^{-3} \int_0^{\nu_m} V \nu^2 d\nu &= 3N, \\ C^3 &= \frac{4\pi V}{3N} \nu_m^3 = \frac{4\pi U}{3} \nu_m^3. \end{aligned} \quad . \quad . \quad (20)$$

Substituting the value of E_ν from equation (14) gives

$$M = \frac{3S^2}{2\mu\nu_m^3} \int_0^m \left[\frac{h\nu}{\exp(h\nu/kT) - 1} + \frac{1}{2}h\nu \right] d\nu$$

or, with the substitutions $\Theta = h\nu_m/k$, $x = \Theta/T$, $y = h\nu/kT$,

$$M = \frac{3h^2S^2T}{2\mu k\Theta^2} \psi(x)$$

where
$$\psi(x) = \frac{1}{x} \int_0^x \frac{y dy}{\exp(y) - 1} + \frac{x}{4} \quad (21)$$

The integral occurring in $\psi(x)$ is not expressible in finite terms, but a table from which it may be obtained is given by Debye (1914) and in the *Internationale Tabellen*, p. 574. A selection of values of $\psi(x)$ is given in table I. The quantity Θ is the same as the 'characteristic temperature' occurring in the Debye theory of heat capacity. For x less than unity (temperatures greater than the characteristic temperature) $\psi(x)$ is nearly constant, and

$$M = \frac{3h^2}{2\mu k} S^2 \cdot \frac{T}{\Theta^2} \quad (22)$$

within three per cent. For greater accuracy in this range the expression

$$\psi(x) = 1 + x^2/36 \quad (23)$$

may be used.

6. Equation (11) for the diffuse intensity $H_2(u, v, w)$ is more or less rigorous, but it is difficult to proceed further with it without making approximations. At not too high temperatures $\exp(P_m)$ in equation (9) for W_m may be replaced by $1 + P_m$, giving

$$W_m = \exp(-2M)P_m \quad (24)$$

One can then evaluate P_m in terms of the amplitudes of the normal co-ordinates, much as was done for M , and obtain $H_2(u, v, w)$ from equation (12). The whole process really amounts to finding the Fourier transform of $\langle A_\nu^2 \rangle$ and then finding the Fourier transform of the result, giving

$\langle A_v^2 \rangle$ again. The intensity at u, v, w is then proportional to $\langle A_v^2 \rangle$, with v satisfying the relation

$$v^2/C^2 = u^2/a^2 + v^2/b^2 + w^2/c^2.$$

The same result can, however, be obtained by a more elementary argument based on the treatment of a sinusoidally-distorted crystal in the previous chapter, and as

TABLE I

Values of the function $\psi(x)$

x	0	1	2	3	4	5
$\psi(x)$	1.000	1.028	1.107	1.233	1.388	1.571
x	6	7	8	9	10	
$\psi(x)$	1.771	1.984	2.205	2.433	2.664	

space does not permit including both methods the simpler will be given.

From the point of view of the X-rays each elastic wave traversing the crystal is equivalent to a sinusoidal distortion of the lattice. It has been shown that a sinusoidal distortion in the x direction of amplitude $L\delta/2\pi a$ and wavelength L produces a pair of satellite spots accompanying each reciprocal-lattice point at actual distances of $\pm 1/L$ from it and of intensity $(L\delta h/2a^2)^2$ smaller. This result has now to be generalized in two ways. If the wave normal is not parallel to the x axis, the satellite spots will be displaced from the point of the reciprocal lattice along a line parallel to the wave normal, not along a line parallel to the x axis. Secondly, it is the component of the displacement in the hkl direction that produces the scattering round the point hkl of the reciprocal lattice, so that the effective amplitude of the wave is its actual amplitude multiplied by the cosine of the angle between the hkl direction and the displacement direction. A wave of amplitude A and length L will therefore produce satellite spots of intensity proportional to $(\pi \Gamma AS)^2$, where Γ is the cosine of the angle between the displacement direction and the hkl direction, and $S = 2 \sin \theta/\lambda$ is the distance of the point hkl from the

origin of the reciprocal lattice, the spots lying at distances of $\pm 1/L$, measured along the wave normal, from the point hkl . This reduces to the earlier result for a wave of amplitude $L\delta/2\pi a$ with its wave normal along the x axis. For a given value of L there are three waves of different frequencies, speeds, amplitudes, and directions of displacement. The intensity at a distance s in a given direction from the point hkl will thus be proportional to

$$\pi^2 S^2 (I_1^2 A_1^2 + I_2^2 A_2^2 + I_3^2 A_3^2), \quad (25)$$

where quantities belonging to the three waves are distinguished by the subscripts 1, 2, 3. In calculating M we could assume that one of the three waves produced a displacement in the hkl direction and the other two at right angles to this direction, but here we have not assumed isotropy of the crystal, and all three must be taken into account. The average values of the squares of the A 's are given by equation (17), so that the intensity is proportional to

$$\begin{aligned} & \frac{S^2}{2N\mu} \left[\frac{I_1^2 E_1}{\nu_1^2} + \frac{I_2^2 E_2}{\nu_2^2} + \frac{I_3^2 E_3}{\nu_3^2} \right] \\ &= \frac{S^2}{2N\mu s^2} \left[\frac{I_1^2 E_1}{C_1^2} + \frac{I_2^2 E_2}{C_2^2} + \frac{I_3^2 E_3}{C_3^2} \right], \quad (26) \end{aligned}$$

where the ν 's and C 's are the frequencies and speeds of the three vibrations of wave-length L . This expression gives the intensity at s as a fraction of the intensity at the point of the reciprocal lattice, which is $N^2 F^2$, or $N^2 F^2 \exp(-2M)$ when allowance is made for the temperature motion. The three waves travelling in the opposite direction will contribute an equal amount, so one would expect the intensity at u, v, w to be given by

$H_2(u, v, w)$

$$= \frac{NF^2 \exp(-2M)}{\mu} \cdot \frac{S^2}{s^2} \cdot \left[\frac{I_1^2 E_1}{C_1^2} + \frac{I_2^2 E_2}{C_2^2} + \frac{I_3^2 E_3}{C_3^2} \right], \quad (27)$$

where $s^2 = u^2/a^2 + v^2/b^2 + w^2/c^2$ for an orthogonal lattice.

The correctness of the proportionality factor can be verified by showing that the total diffuse intensity is equal, to the first order in M , to the intensity lost by the central spot. On the Debye theory there is a maximum value of ν , independent of direction in the crystal, and hence the cloud of diffuse scattering is spherically symmetrical, and stops abruptly at a limiting value of s . For the purpose of checking the proportionality factor we may ignore the differences between the E 's and C 's, and take the total diffuse intensity to be the integral of equation (27) over the interior of a sphere of reciprocal space of radius ν_m/C . The sum of the I 's will be unity under these conditions, and the total diffuse intensity becomes

$$\begin{aligned} \iiint H_2(u, v, w) du dv dw &= abc \iiint H_2(u, v, w) d(u/a) d(v/b) d(w/c) \\ &= U \int_0^{\nu_m/C} H_2(s) \cdot 4\pi s^2 ds \\ &= \frac{NUF^2 \exp(-2M)}{\mu} \cdot S^2 \cdot \int_0^{\nu_m/C} \frac{E_v}{C^2 s^2} 4\pi s^2 ds, \end{aligned}$$

or, since $s = 1/L = \nu/C$ and $NU = V$,

$$\begin{aligned} &\frac{VF^2 \exp(-2M)}{\mu} \cdot S^2 \cdot \frac{4\pi}{C^3} \cdot \int_0^{\nu_m} E_v dv \\ &= F^2 \exp(-2M) \cdot 2MN, \end{aligned} \quad (28)$$

by equation (19). The reduction of the total intensity of the central spot is

$$NF^2 - NF^2 \exp(-2M), \quad (29)$$

which is the same as equation (28) to the first order in M . Agreement to higher orders cannot be expected, because of the approximations made in deriving equation (27).

7. Equation (27) shows that the intensity of the thermal scattering increases with increasing order of reflection (S^2), decreases with increasing distance from the points of the reciprocal lattice ($1/s^2$), and for temperatures greater than Θ

varies like $S^2T \exp(-KS^2T)$, where K is independent of T and (to the Debye approximation) the indices of reflection. It would thus have a maximum value for $S^2T = 1/K$. The approximations made, which are equivalent to the expansion of $\exp(P_m)$ to obtain equation (24), would hardly be valid for such large values of S^2T , but it seems likely that the predicted behaviour is qualitatively correct, and that the intensity of reflection in the regions near the points of the reciprocal lattice does ultimately decrease with increasing temperature or order of reflection (Born, 1942-3, p. 317). The factor in brackets, involving the speeds of propagation of the vibrations, is in general strongly dependent on the direction of s and on the point of the reciprocal lattice concerned. It has been worked out for cubic crystals by Jahn (1942), but the expressions are too complicated to be quoted and discussed here.

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